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TWELFTH ARCTIC AND
MARINE OIL SPILL PROGRAM
TECHNICAL SEMINAR**

**COMPTE RENDU: DOUZIÈME COLLOQUE
TECHNIQUE DU PROGRAMME DE LUTTE
CONTRE LES DÉVERSEMENTS
D'HYDROCARBURES EN MER ET DANS
L'ARCTIQUE (AMOP)**



**JUNE 7-9, 1989
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**Twelfth Arctic and Marine Oilspill
Program Technical Seminar**

**Douzième colloque technique du
programme de lutte contre les
déversements d'hydrocarbures dans
l'arctique**

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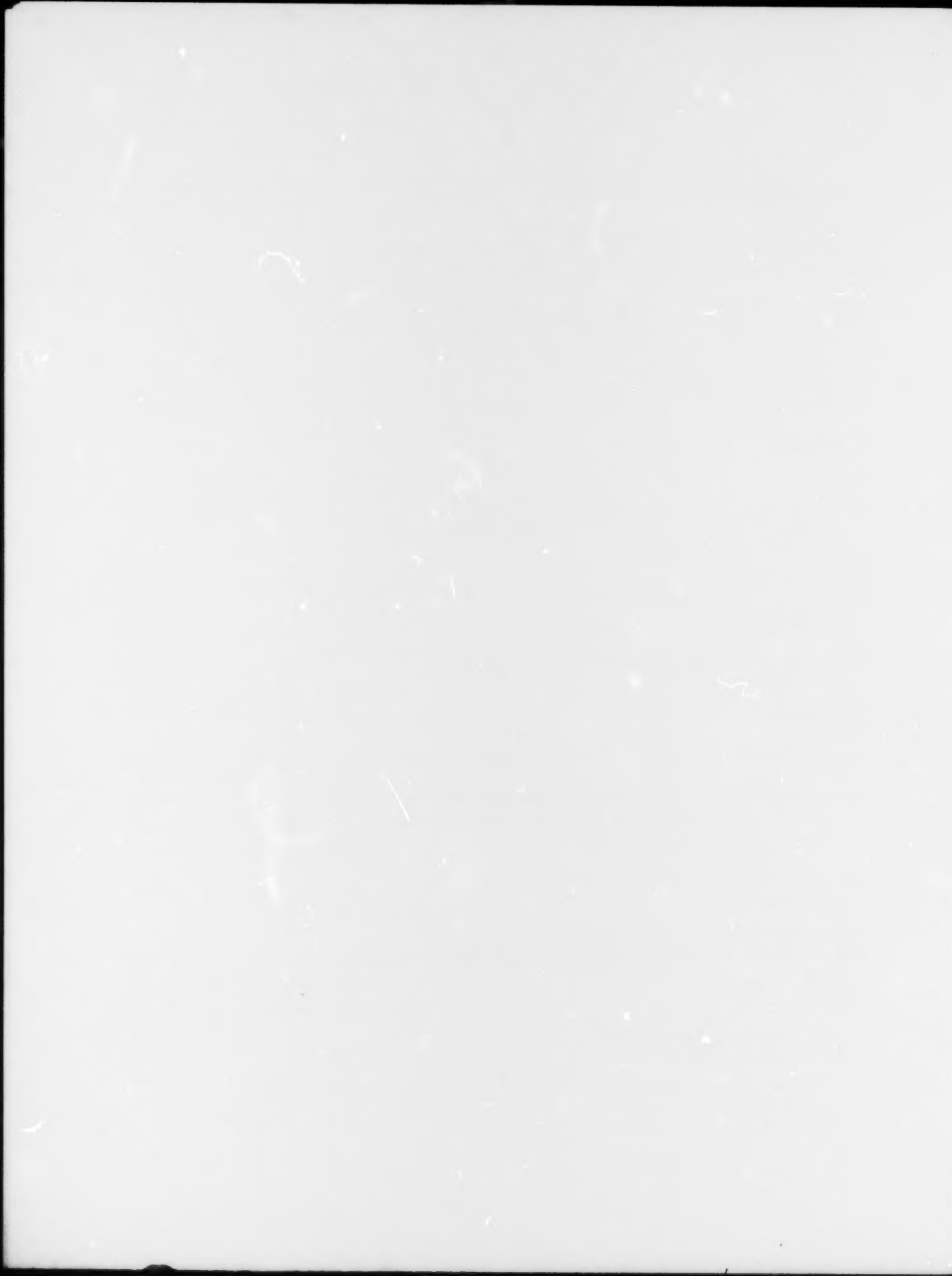
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SMOKE PLUMES FROM CRUDE OIL BURNS

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ABSTRACT

Measurements of optical properties and particle agglomeration of smoke from Alberta Sweet Blend Mix crude oil fires were made using a one cubic meter aging/dilution chamber. Measurements were made at ambient temperature simulating conditions in dilute smoke plumes away from the fire and at 100°C which simulates temperature conditions within several flame heights above the burning crude oil. Measurements of light transmission at three different wavelengths through the smoke collected in the chamber proved that the specific extinction coefficient of the carbonaceous agglomerate particles in the smoke is independent of the agglomerate size. These data are used as input to a calculation of smoke particle settling from the fire plume and deposition remote from the fire site. The calculation uses a large eddy simulation method to predict characteristics of wind blown buoyancy driven fire plumes. The calculation is capable of displaying the major features of smoke transport from the site of crude oil combustion. The process of smoke particulate settling from the plume is considered in detail by tracking representative smoke particles in the calculation. Results of example calculations are presented that demonstrate important features of the method.

BACKGROUND

In 1985, the Center for Fire Research (CFR) at the U.S. National Institute of Standards and Technology (NIST) began studies of oil spill combustion under support from the Minerals Management Service (MMS) of the U.S. Department of the Interior. This work seeks to quantify the processes involved in oil spill combustion on open waters and in water filled channels formed in broken ice including measurements of smoke production and prediction of smoke dispersal. Additional technical support from Environment Canada has allowed the study to be broadened in scope to include chemical analysis of the oil, oil residue, and oil smoke.

At the beginning of this research program it had already been demonstrated by other investigators that burning was an efficient means of removing crude oil from the surface of the water under a variety of conditions. Experimental burns of oil in ice leads (channels of water through ice) conducted by Brown and Goodman [1] and Smith and Diaz [2] showed that 50% to 90% of an oil spill could be removed by burning. In tests in which oil pools were free to spread during burning, Buist and Twardus [3] report consumptions of 70% to 90%. The focus of the research program at NIST was to quantify the combustion process and in particular measure properties of the smoke from the crude oil fires.

The goal of the NIST research program is to provide measurements and means to make quantitative predictions of (a) the fraction of oil in a spill

that can be consumed by an in-situ combustion process, (b) the characteristics of the residual oil, and (c) the characteristics of the combustion product flow from the burning oil in the atmosphere. It is anticipated that this information may be cast into a form that is usable by local officials and oil spill response professionals as part of the decision making process in the event of an oil spill.

In the first year of the study [4], the burning process was studied at two pool diameters, 0.6 m and 1.2 m. The emission rate, size distribution, and specific extinction coefficient (relative blackness) were measured for the smoke produced by the fires. The structure of the smoke agglomerates was examined by electron microscopy. The burn residue left on the water by natural quenching of the combustion was analyzed and found to be depleted of short chain alkanes and cycloalkanes when compared with the fresh crude oil. A calculation of the induced air flow into a distribution of pool fires simulating the simultaneous burning of oil in many separate ice leads was performed to demonstrate the magnitude of the fire induced wind at ground level.

In the second year [5], extensive measurements of polynuclear aromatic hydrocarbon (PAH) content of the crude oil and the smoke were performed in close cooperation with Environment Canada. Measurements showed that about 10% of the crude oil was converted to smoke in the combustion process. A methodology was developed to predict the down wind dispersal of smoke generated by one or more oil spill fires in close proximity.

Last year [6], smoke emission was measured during the burning of oil layers thin enough to cause boiling in the supporting water layer. Under these conditions both smoke emission and the PAH content of the smoke was reduced compared to burning of thicker layers. Measurements of the optical properties and sedimentation velocities for aged and diluted smoke samples were performed. These characteristics are important in estimating smoke properties downwind of the oil spill fire. Analyses of smoke dispersal in the atmosphere were continued by formulating a model for smoke particle settling time which determines soot deposition on the ground remote from the combustion site.

This year measurements have focussed on the determination of the agglomeration rate for smoke particles at both ambient temperature conditions, which corresponds to the cooler, diluted smoke in the plume and at a temperature around 100°C, which corresponds to the temperature several flame heights above the fire. The plume dynamics model, that was started last year, is continued with a formulation in terms of buoyancy induced vortex trajectories (which represent the large scale plume turbulence) so that the agglomeration rate inferred from the laboratory measurements can be incorporated in the plume model. In the laboratory study, the agglomerate size increases with holding time in the aging/dilution collection chamber, while in a steady state plume model, the agglomerate size increases with downwind position along the plume, since downwind distance plays the role of time.

SMOKE AGING

As smoke rises in a plume from the burning oil, the smoke particles in the hot, fresh smoke collide and stick together forming larger particles. Downstream in the plume, changes also occur in the cooler, diluted smoke. As was shown in the 1986 report by Evans et al. [4], an individual smoke particle has a loose packed agglomerate structure made up of nearly spherical subunits with a typical diameter of about 50 nm. The colliding particles are actually agglomerates. Most particle growth studies have focussed on liquid droplets, which maintain a spherical shape after collisions, and these results are not applicable to agglomerate type structures. There is no data on the agglomeration rate for crude oil smoke.

Theoretical studies by Jones [7] and by Berry and Percival [8] lead to the conclusion that the spherical subunits in agglomerates absorb light as though they act independently of the agglomerate. This implies that the extinction coefficient per unit mass concentration of smoke is a constant independent of the agglomerate size, since light extinction is primarily a result of light absorption for carbonaceous particles. This prediction was tested by monitoring the specific extinction coefficient of smoke at three wavelengths as the smoke in the chamber agglomerates. The optical properties are required to calculate the absorption and scattering of solar radiation by the smoke.

The design of the aging/dilution facility was described in the 1988 Report by Evans et al. [5]. The key design features of the facility include rapid filling of the chamber in less than a minute, uniformly heated wall temperature up to 150°C, large volume (1 m³) allowing aging for over an hour without significant wall loss, and a 100 liter piston allowing the volume of the chamber to be reduced as the smoke is extracted without the need of adding makeup air. The smoke collection system and the aging dilution system are illustrated in Figure 1.

The experiment consisted of burning Alberta Sweet crude oil floating on water in a 60 cm diameter pan. The smoke moving up the duct is mixed by a tripper plate and then is drawn isokinetically through a 10 cm sampling probe into the chamber. A fan continuously draws smoke through the chamber until the chamber is filled, then the two stainless steel butterfly valves, one on the inlet and one on the outlet, are simultaneously closed to capture a 1 m³ sample. The smoke temperature in the stack is about 100°C, which is close to the chamber temperature for the high temperature aging experiments. In the case where the chamber is maintained at ambient conditions, it takes about 4 minutes for the gas to equilibrate to the wall temperature. A significant amount of cooling occurs as the gas is transported through the sampling line.

The number and mass concentration are monitored throughout the experiment. The mass concentration is monitored with a tapered-element oscillating microbalance (TEOM), which consists of a filter disk attached to the top of a hollow, oscillating tube. The mass concentration is determined from the flow rate through the tube and the change in the frequency of the tube oscillation as the smoke is deposited. This instrument allows continuous readout of smoke concentration. The number concentration is monitored by a

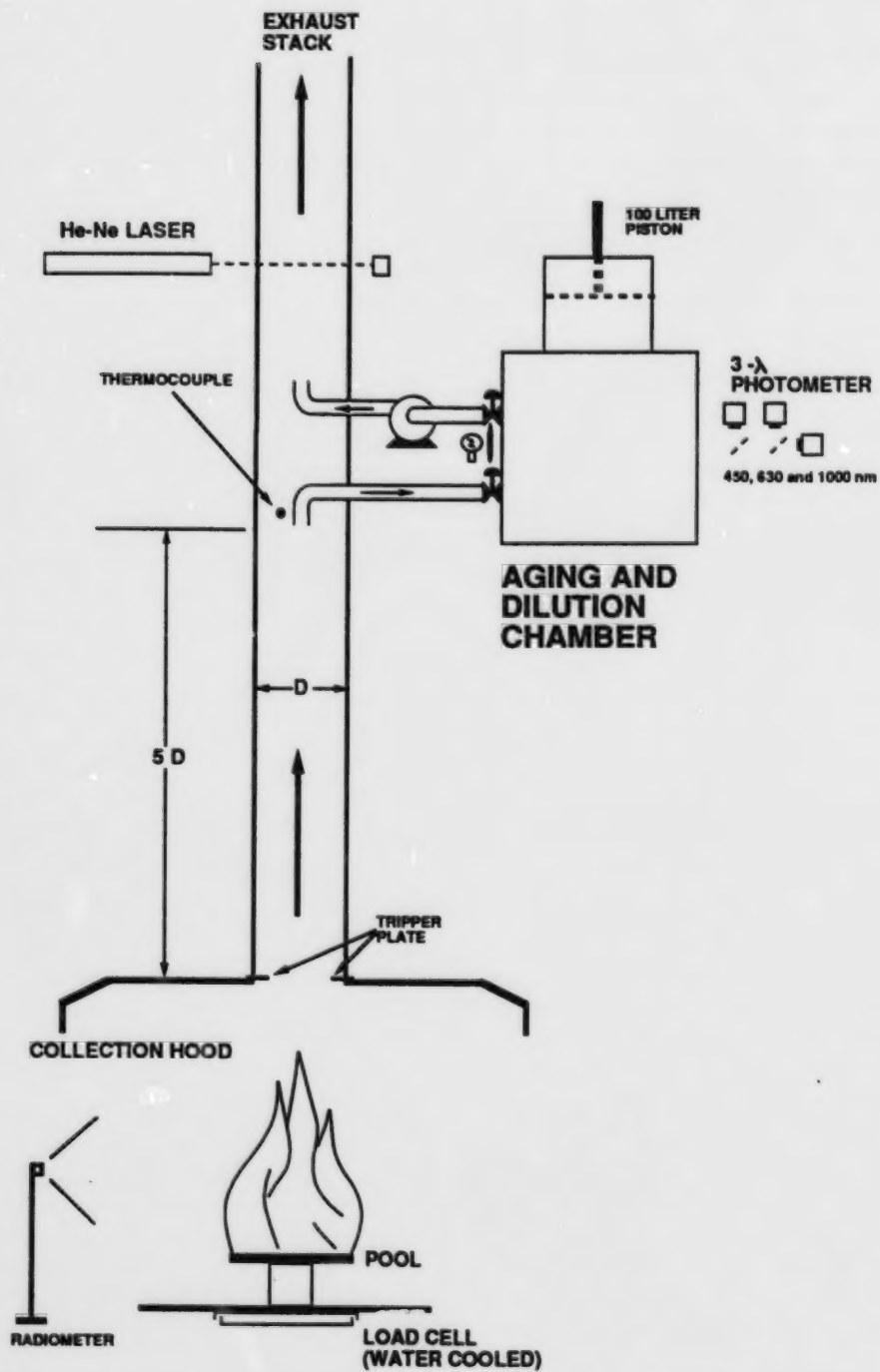


Figure 1. Schematic of the smoke collection system and aging dilution facility for crude oil burns.

continuous flow condensation nucleus counter (CNC), which utilizes butanol as the condensing vapor. The smoke is saturated with butanol as it flows above a reservoir of butanol heated to 30°C. Then the smoke flows through a cooled tube in which the vapor condenses on the smoke producing micrometer size butanol droplets. These droplets are counted optically by light scattering. The CNC gives a continuous readout of the number concentration of the smoke. The smoke is diluted by a factor of about 60 before entering the CNC to keep the concentration below 3.0×10^5 particles/cm³, the saturation level of the instrument.

The number concentration begins at about 10^7 particles/cm³ and decreases by a factor of about 50 over a 90 minute period as indicated in Figure 2. Most of this decrease is a result of particle agglomeration rather than wall loss, since over the same period of time the mass concentration decreased by a factor of two or less (Figure 3). The average mass of the agglomerate increases by about a factor of 30 as indicated in Figure 4. Assuming a primary particle size of 50 nm and a primary particle density of 2.0 g/cm³, this change in mass corresponds to an increase in the number of primary units per agglomerate from about 200 at the initial time to a final value of about 6000.

The rate constant for agglomeration, Γ , is defined by the equation:

$$dN/dt = -\Gamma N^2, \quad (1)$$

where N is the number concentration of the agglomerates in terms of particle/cm³. If Γ is assumed to be a constant, then equation (1) can be integrated to give

$$1/N - 1/N_0 = \Gamma t, \quad (2)$$

where N_0 is the initial number concentration. The plot of $1/N$ versus time in Figure 5 shows a linear behavior for times less than about 30 minutes. The curvature at later times is at least partly a result of particle loss to the walls becoming a significant factor at long times. Table 1 summarizes the experimental results for the agglomeration rate based on a linear least square fit of the data over the initial 10 to 20 minutes of each experiment. The values of Γ from repeat experiments differ by only a few percent; however, the uncertainty in the absolute value is large. We estimate the values of Γ to be $8 \pm 4 \times 10^{-10}$ cm³/s for ambient conditions and $13 \pm 7 \times 10^{-10}$ cm³/s for a temperature around 100°C. The sources of the uncertainty include the lack of an aerosol particle concentration standard, the reduced accuracy of the CNC from operation near saturation, and the use of a diluter. There is an additional uncertainty for the high temperature experiments resulting from thermophoretic particle losses as the warm smoke flows through the cool tube. The gas temperature drops from about 100°C to ambient conditions as the particles reach the CNC. The particle losses could be as large as 25%, which would reduce the agglomeration coefficient from about 13×10^{-10} cm³/s to about 10×10^{-10} cm³/s.

The light intensity transmitted through the aging dilution chamber was monitored at three wavelengths, 450, 630, and 1000 nm, using a photometer system designed by Cashdollar [9]. The specific extinction coefficient, σ ,

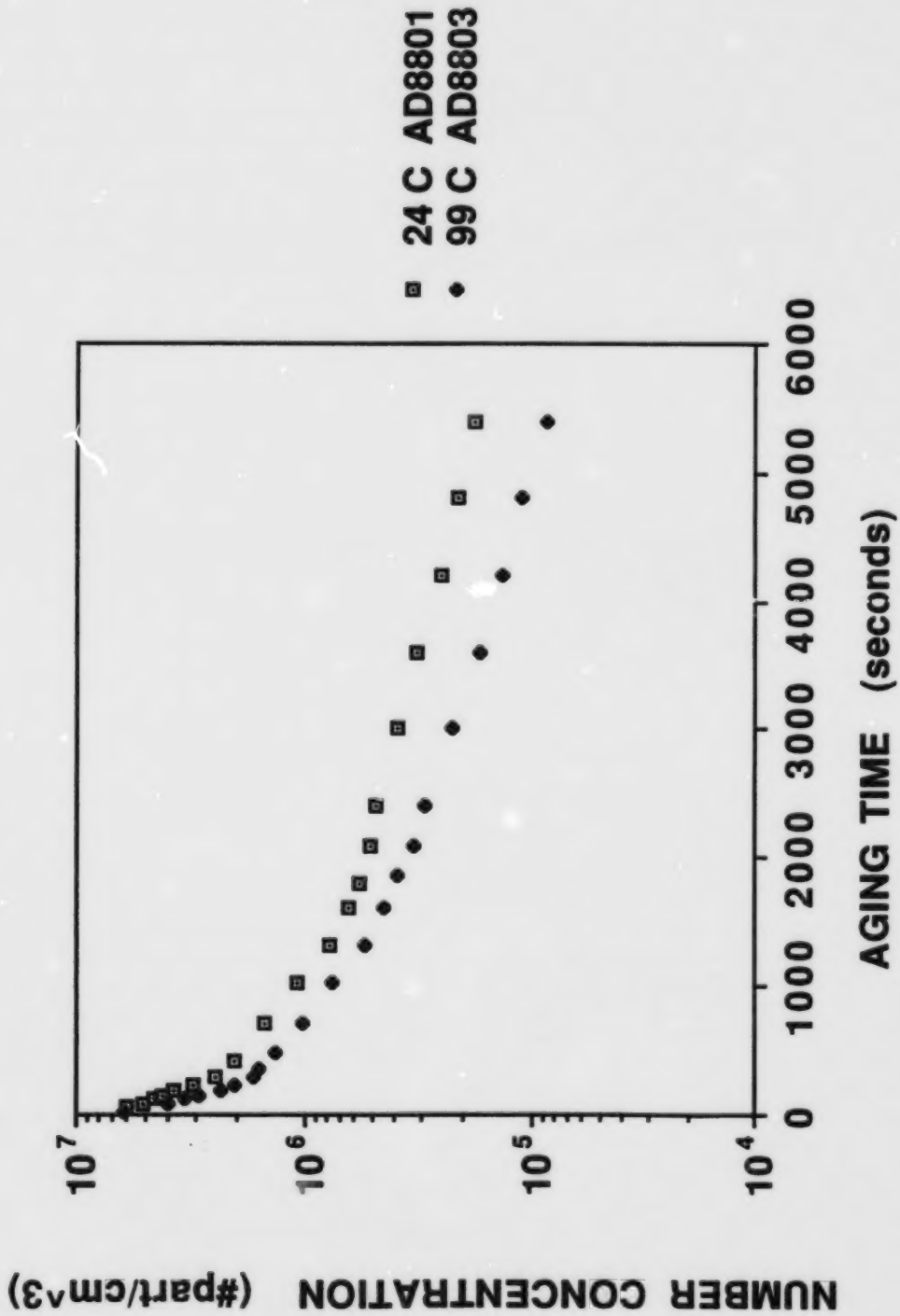


Figure 2. Number concentration versus time for aging of crude oil smoke at ambient and at elevated temperatures.

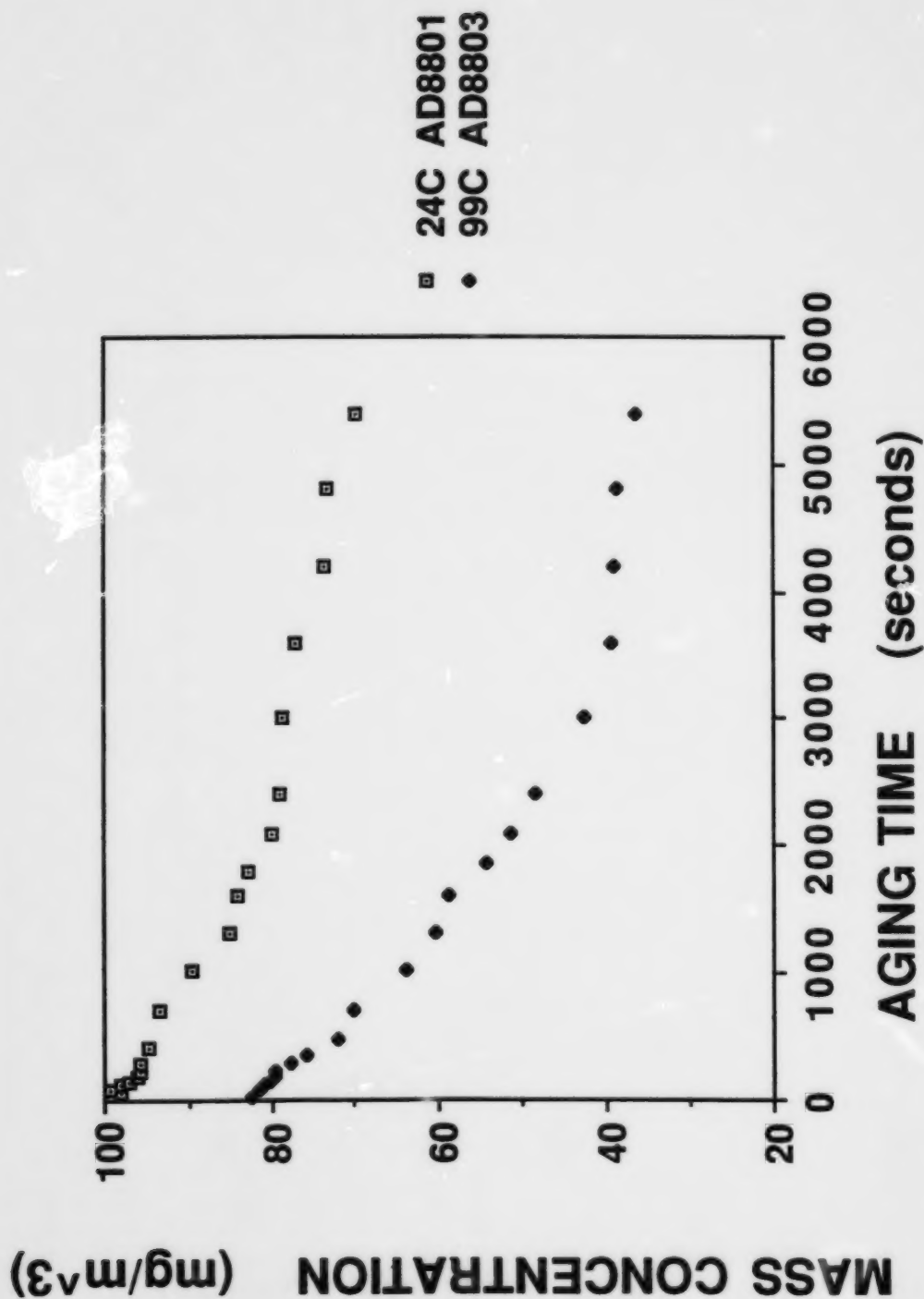


Figure 3. Mass concentration versus time for aging of crude oil smoke at ambient and at elevated temperatures.

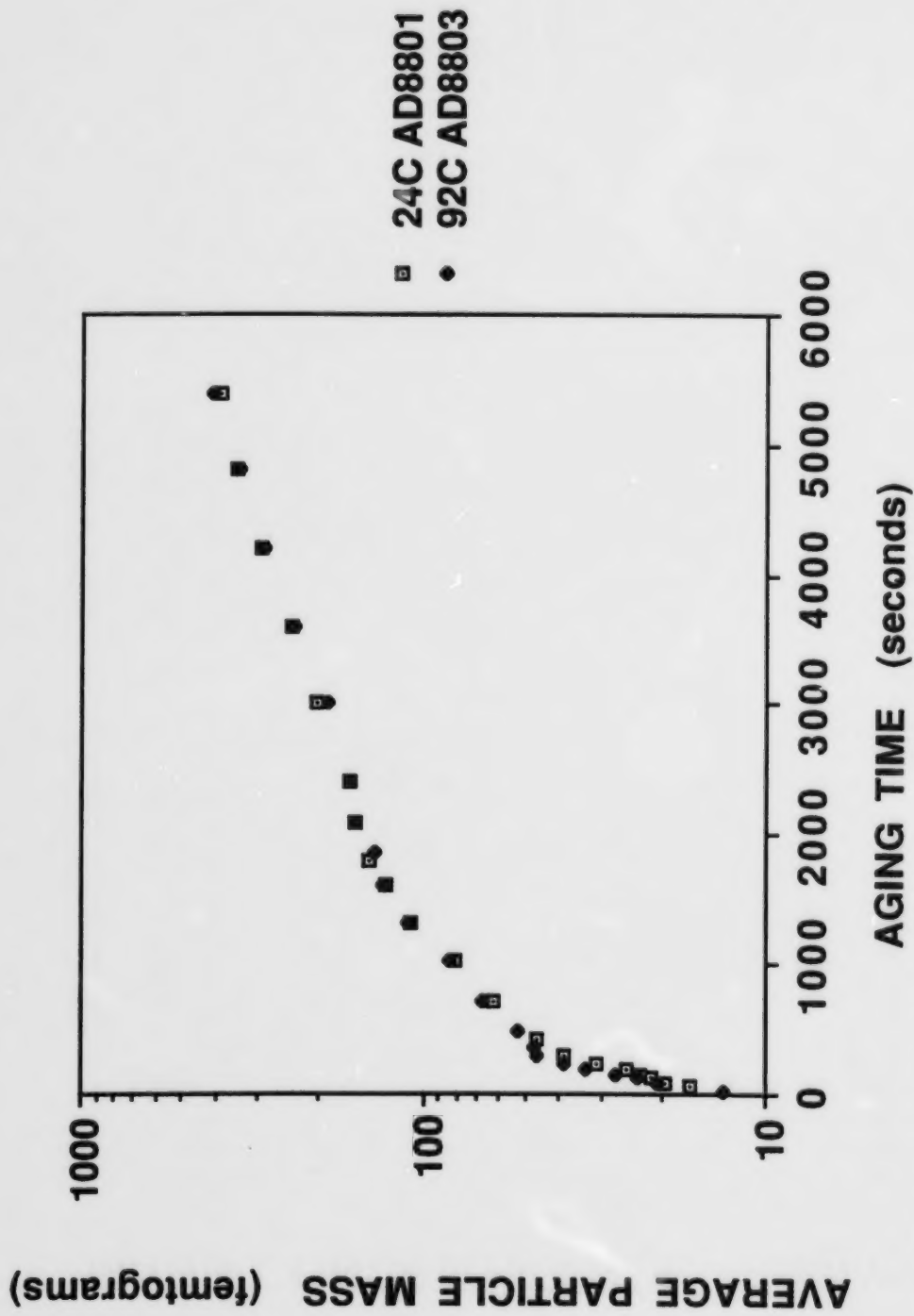


Figure 4. Average particle mass as a function of time for aging of crude oil smoke at ambient and at elevated temperatures.

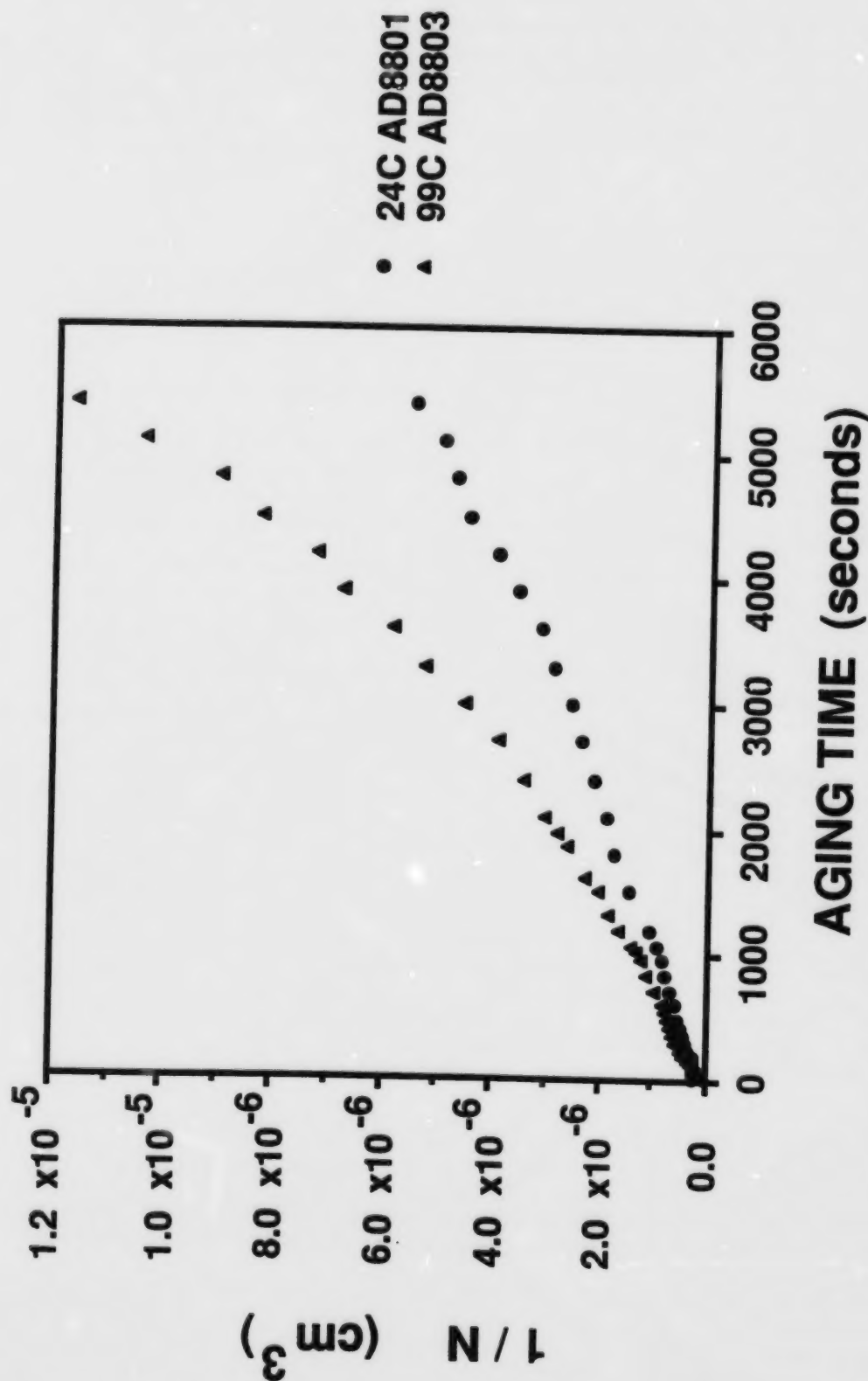


Figure 5. $1/\text{Number Concentration}$ versus time for aging of crude oil smoke at ambient and at elevated temperatures. The slope at small times is used for determining the coagulation coefficient.

Table I Agglomeration Rates For Smoke at Ambient Temperature
and at Elevated Temperature

Run #	Temperature K	Fitting interval seconds	N_0 cm^{-3}	Γ cm^3/s
8801	297	60 - 720	6.0×10^6	7.9×10^{-10}
8805	297	30 - 1320	7.7×10^6	7.6×10^{-10}
8804	365	30 - 720	4.7×10^6	13.2×10^{-10}
8803	372	30 - 480	6.2×10^6	13.1×10^{-10}

Table II Average Values of Specific Extinction Cross-Section, σ

Run #	Temperature K	Time Interval seconds	$\sigma(450)$ m^2/g	$\sigma(630)$ m^2/g	$\sigma(1000)$ m^2/g
8801	297	30 - 5400	9.7	7.8	5.1
8805	297	30 - 5400	9.0	7.3	4.7
8804	365	30 - 5400	9.4	7.6	5.0
8803	372	30 - 4200	10.7	8.6	5.6
<u>Avg. σ</u>			9.7 ± 0.7	7.8 ± 0.6	5.1 ± 0.4

was obtained from the ratio of the extinction coefficient to the mass concentration of smoke as monitored by the TEOM. The value of σ did not change significantly over a 90 minute aging period for either the ambient temperature smoke or the hot smoke as shown in Figure 6. There was not a significant effect of the temperature of the smoke on the value of σ as shown in Table II. The results for σ for the four experiments are $5.1 \pm 0.4 \text{ m}^2/\text{g}$ (1000 nm), $7.8 \pm 0.6 \text{ m}^2/\text{g}$ (630 nm), and $9.7 \pm 0.7 \text{ m}^2/\text{g}$ (450 nm). These results are similar to the preliminary results presented in last years report by Evans et al. [5]. The variability in the TEOM performance is thought to be the main cause of the experimental uncertainty. This is supported by the observation that the variation in the ratio of the transmitted intensities for two wavelengths is less than 2% for all four tests. That is, the experimental variability is not caused by test to test variability in the smoke properties, but rather variability in the TEOM performance.

DISCUSSION OF SMOKE AGING

Mountain et al. [10] and Mulholland et al. [11] report computer simulations of the smoke agglomeration rate for the limiting cases of free molecular dynamics, in which the particle size is small compared to the mean free path of the gas, and continuum flow, in which the particle size is large compared to the mean free path of the gas. The experimental conditions approach continuum flow in terms of the agglomerate size, though there could still be a non-continuum effect arising from the primary particle size being smaller than the gas mean free path. The experimentally observed linear dependence of $1/(\text{number concentration})$ on time is consistent with the continuum flow prediction; whereas, the free molecular flow leads to a quadratic dependence on time. The model predictions for the agglomeration rate for clusters composed of 200 primary units is based on a primary sphere size of 50 nm. The free molecular model leads to Γ equal to $3.0 \times 10^{-8} \text{ cm}^3/\text{s}$ at 300 K and $3.3 \times 10^{-8} \text{ cm}^3/\text{s}$ at 370 K. The continuum result for ambient conditions for an average cluster size of 12 is $6.0 \times 10^{-10} \text{ cm}^3/\text{s}$, which is twice the coagulation coefficient of coalescing droplets. The continuum result for relatively small clusters is about 25% less than the observed result for much larger clusters and the free molecular result is about a factor of 40 higher than the measured result.

The predicted temperature dependence of Γ is approximately $(T)^{1/2}$ for both the free molecular and continuum flow condition. The temperature dependence inferred from the experiments is $(T)^{2.4}$. As discussed above, the experimental results for Γ at elevated temperatures are thought to be overestimates as a result of thermophoretic losses in the sampling lines.

PARTICULATE SETTLING ANALYSIS

The purpose of this section is to develop a method for solving the equations which govern the evolution of a smoke particle plume; from the point at which it is injected into the atmosphere until it is finally deposited on the ground. The principal assumptions underlying the model are:

- 1) The fire generating the smoke and hot gases is burning steadily.

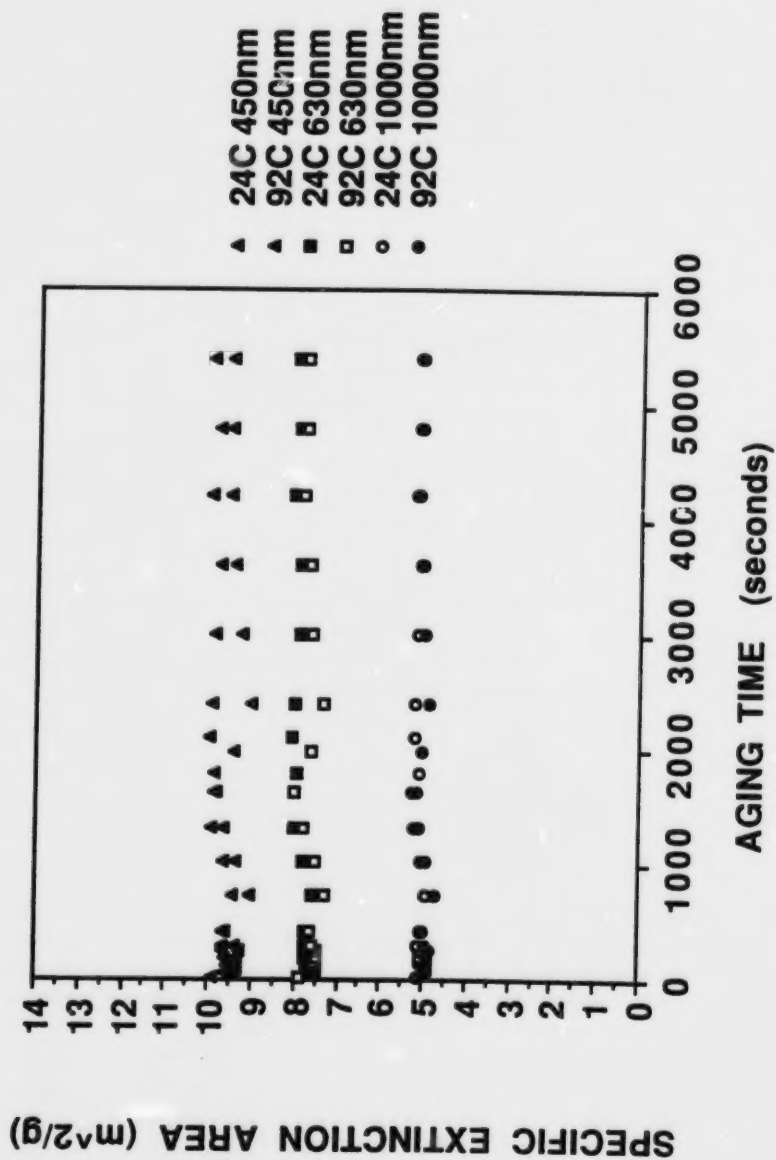


Figure 6. The specific extinction coefficient, σ , for 450 nm, 630 nm, and 1000 nm versus time for aging of crude oil smoke at ambient and at elevated temperatures.

- 2) The injection altitude and particle mass flux associated with the fire are known.
- 3) The gas temperature in the buoyant plume equilibrates with the atmosphere before any significant particle settling begins.
- 4) The ambient wind speed is much larger than the velocities induced by the negatively buoyant smoke particle plume.
- 5) Individual particle settling velocities are much smaller than the collective effects represented by the smoke particle plume.
- 6) The stratification of the atmosphere plays no role in the settling process.

The last assumption limits the injection altitude for which the analysis is valid to at most one kilometer. The determination of the injection altitude itself is not part of this analysis, although it does fit within the framework of the general approach. The goal of the present study is the ability to predict the downwind deposition pattern of the smoke particulate at ground level. The controlling parameters are the injection altitude and initial cross-section area of the plume, the particulate mass flux, and the ambient wind velocity.

To proceed, a cartesian coordinate system X,Y,Z is introduced as shown in figure 7. The variable X increases in the direction of the ambient wind, Z is directed vertically upward, and Y is horizontal coordinate perpendicular to the other two. Let U,V and W be the air velocity components in the X,Y and Z directions respectively. In this model U is the ambient wind speed and is presumed known. The smoke particulate is described in terms of a mass density ρ_p , mass flux M , and initial cross sectional area L^2 . The initial injection altitude H is defined as the distance from the ground level to the initial center of mass of the plume. The atmosphere is characterized by an ambient density ρ_0 and the magnitude of the gravitational acceleration is g . Dimensionless coordinates, velocity components, and smoke density can be introduced in terms of these parameters as follows:

$$\begin{aligned}
 (Y,Z) &= L(y,z) \\
 X &= (LU)^{3/2} / (gM/\rho_0)^{1/2} t \\
 (V,W) &= (gM/(\rho_0 UL))^{1/2} (v,w) \\
 \rho_p &= M/(UL^2)\rho
 \end{aligned}
 \tag{3}$$

The dimensionless horizontal (v) and vertical (w) velocities induced by the settling process, as well as the dimensionless smoke particulate density ρ are functions of the reduced transverse horizontal coordinate (y), vertical coordinate (z), and downwind coordinate (t). This nomenclature is introduced because the mathematical model of this three-dimensional steady state process is equivalent to a two dimensional time dependent process viewed in a cross-sectional plane moving downwind at the ambient wind speed U . Thus, the smoke distribution in the upwind plane $X=X_1$ in figure 7 evolves over a time interval defined by the second of eqs. (3) into the distribution at the downwind station $X=X_2$ in the figure.

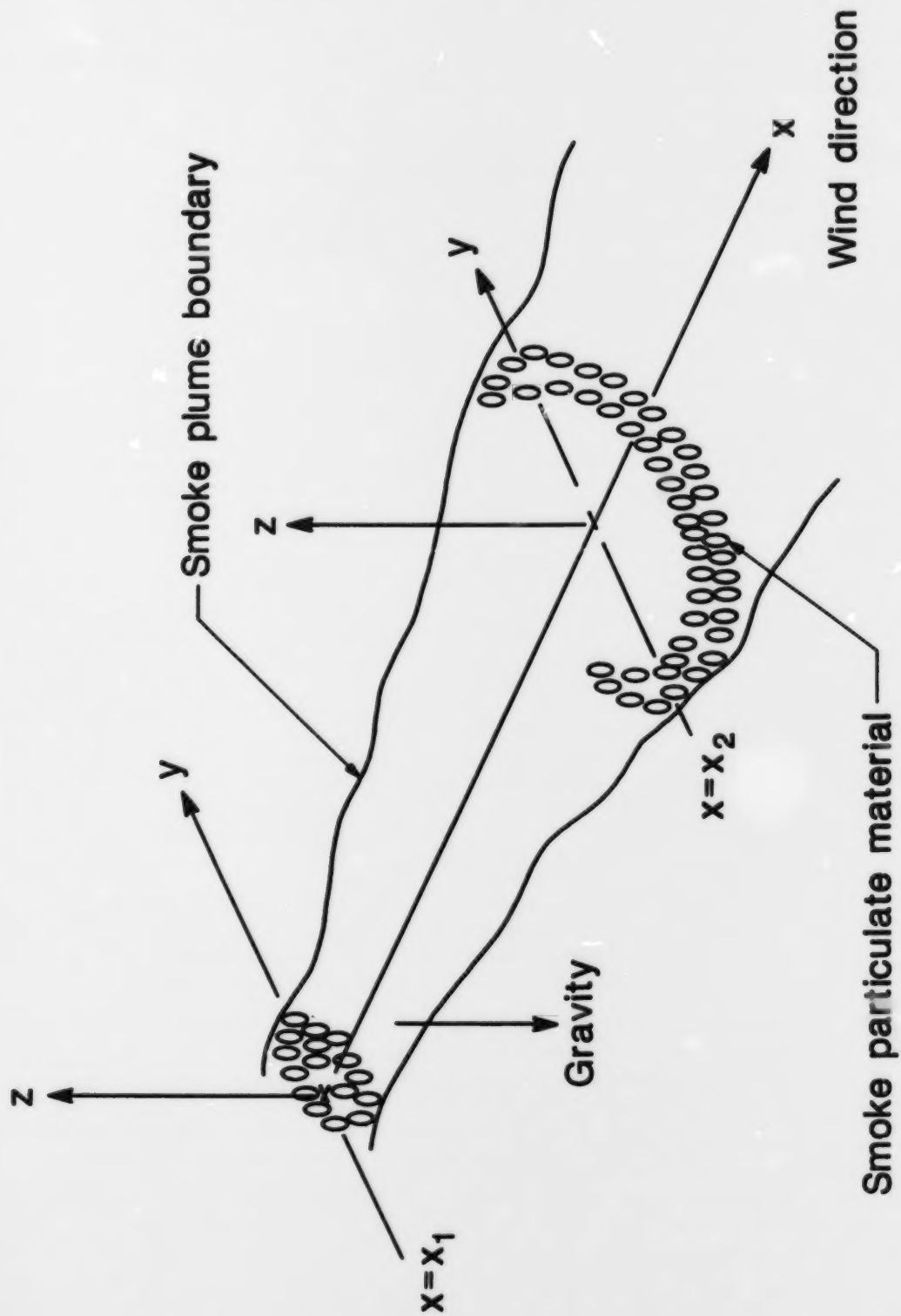


Figure 7. Schematic showing downwind evolution of smoke plume.

It is necessary to follow the particle density downwind until most of the smoke is within some specified small distance of the ground, at which point it can be regarded as having settled out of the system. Since the primary interest is in the location of the smoke particulate matter, the numerical method must focus on the Lagrangian coordinates of the smoke, rather than the general flow field. To this end, it is convenient to replace the continuous model of the smoke density by discrete clumps of matter as shown in figure 8. Each clump of matter carries a specific particulate mass flux and a vorticity which changes with time. The vorticity is induced by horizontal density gradients, with positive gradients inducing negative vorticity as illustrated in figure 8.

The mathematical basis for this discretization is the introduction of a Lagrangian coordinate system. Each clump of matter is characterized by its initial coordinates as follows:

$$\text{at } t = 0; y = y_0; z = z_0$$

Then, the coordinates y, z of each clump are calculated as functions of time as solutions of the differential equations

$$\frac{\partial y}{\partial t} = v(y, z, t) \quad \frac{\partial z}{\partial t} = w(y, z, t) \quad (4)$$

There is one pair of such equations for each clump; i.e. for each value of y_0, z_0 . To generate the velocity fields, the evolution equations for the vorticity (the local angular velocity in the atmosphere) and density, need to be rewritten in terms of the new coordinate system. The appropriate formulae are:

$$\rho = f(y_0, z_0) \quad (5)$$

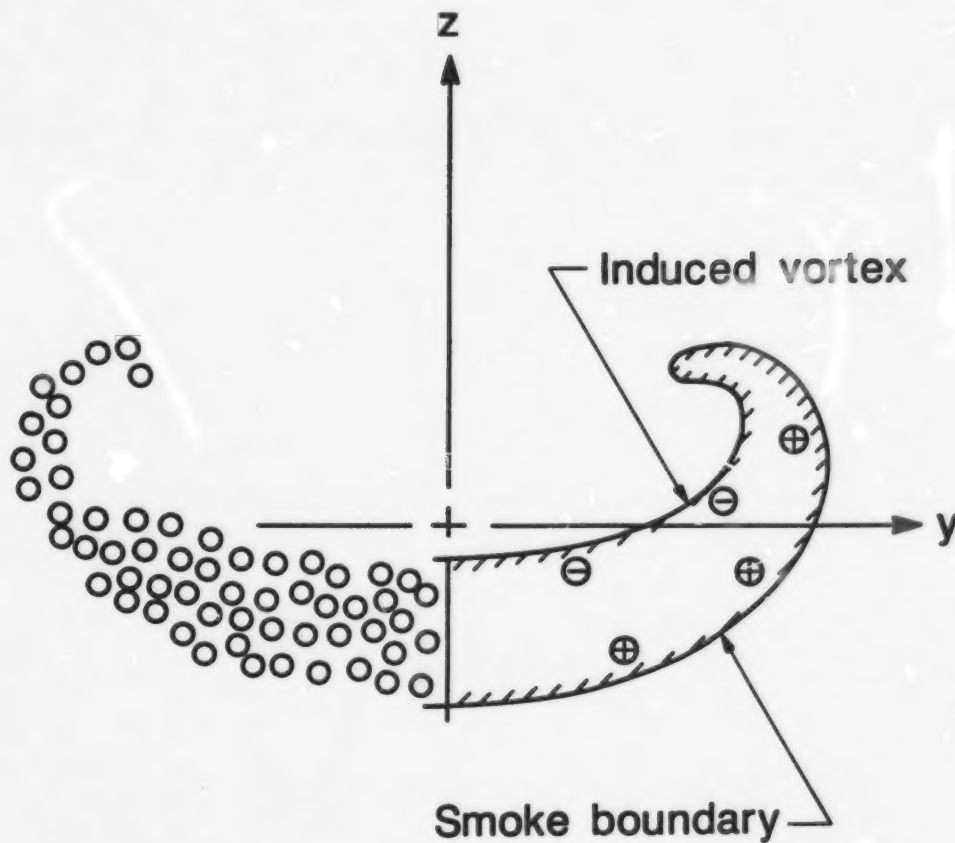
$$\frac{\partial \omega}{\partial t} = S \frac{\partial f}{\partial z_0} - T \frac{\partial f}{\partial y_0}$$

Here, the quantity ω is the vorticity while $f(y_0, z_0)$ is the initial upwind density distribution, and the density does not change in this system of coordinates. This is the mathematical statement of the fact that the mass flux associated with each clump is always the same as the clump progresses downwind.

The generation of the vorticity fields involves four coordinate gradients which describe the mixing and stretching of the fluid by the vortices. These quantities, denoted Q, R, S , and T are defined as follows:

$$\begin{aligned} \frac{\partial y}{\partial y_0} &= Q(y_0, z_0, t) & \frac{\partial y}{\partial z_0} &= R(y_0, z_0, t) \\ \frac{\partial z}{\partial y_0} &= S(y_0, z_0, t) & \frac{\partial z}{\partial z_0} &= T(y_0, z_0, t) \end{aligned} \quad (6)$$

To preserve the accuracy of this method, it is important not to actually compute any spatial derivatives numerically. To avoid this, we note that analytical recipes for $v(y, z, t)$ and $w(y, z, t)$ can be generated and that these



⊕ Positive vorticity
⊖ Negative vorticity

Figure 8. Discretization of smoke into vorticity containing clumps. Horizontal density gradients induced vorticity.

recipes can be exactly differentiated. The procedure for generating these recipes will be indicated briefly below. Given the existence of such expressions, however, it is easy to generate evolution equations for Q, R, S, and T. The necessary equations are:

$$\begin{aligned}
 \frac{\partial Q}{\partial t} &= Q \frac{\partial v}{\partial y} + S \frac{\partial v}{\partial z} \\
 \frac{\partial R}{\partial t} &= R \frac{\partial v}{\partial y} + T \frac{\partial v}{\partial z} \\
 \frac{\partial S}{\partial t} &= Q \frac{\partial w}{\partial y} + S \frac{\partial w}{\partial z} \\
 \frac{\partial T}{\partial t} &= R \frac{\partial w}{\partial y} + T \frac{\partial w}{\partial z}
 \end{aligned} \tag{7}$$

Equations (4), (5), and (7) constitute a set of seven ordinary differential equations and one algebraic statement that must be solved to describe the evolution of each clump. They are equivalent to solving the equations of fluid motion everywhere in space. Obviously, any method which attempts to solve the equations everywhere is going to yield a much cruder approximation to the quantities of interest than one which concentrates attention directly on the area occupied by smoke. Thus, it is worthwhile to expend this much effort on tracking the fate of a single clump of particulate matter, if no resources have to be devoted to calculating quantities outside the smoke cloud.

The final piece of information required to implement this method is the explicit representation of the velocities in terms of the coordinates y, z . To this end, it is convenient to introduce a stream function $\Psi(y, z, t)$ that is related to the velocities by:

$$\frac{\partial \Psi}{\partial z} = v; \quad \frac{\partial \Psi}{\partial y} = -w \tag{8}$$

The requirement that the velocity fields conserve mass yields an equation for Ψ in terms of ω . The solution can be expressed in terms of a Greens function $G(y, z, y_0, z_0)$ as:

$$\begin{aligned}
 \Psi &= \iint dy_0 dz_0 G(y, z, y_0, z_0) \omega(y_0, z_0, t) \\
 G &= \frac{1}{2\pi} \left\{ \log(r_+) - \log(r_-) - \log(rI_-) + \log(rI_+) \right\} \\
 (r_+)^2 &= (y - y_0)^2 + (z - z_0)^2 \\
 (r_-)^2 &= (y + y_0)^2 + (z - z_0)^2 \\
 (rI_-)^2 &= (y - y_0)^2 + (z + [2(H/L) + z_0])^2 \\
 (rI_+)^2 &= (y + y_0)^2 + (z + [2(H/L) + z_0])^2
 \end{aligned} \tag{9}$$

Physically, the Greens function represents the flow induced by the vortex pair associated with two clumps as shown in figure 9a. The signs of the vortices are such that the direction of the swirling motion, as indicated by the arrows, induces a downward flow. This accounts for the first two terms in

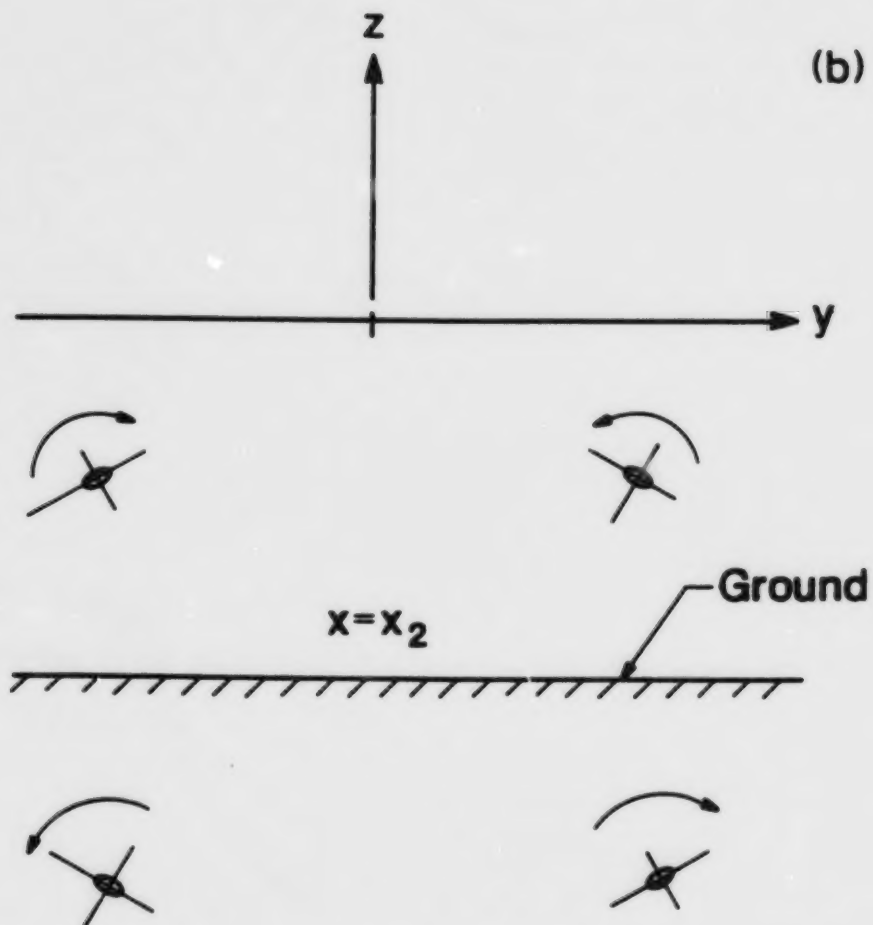
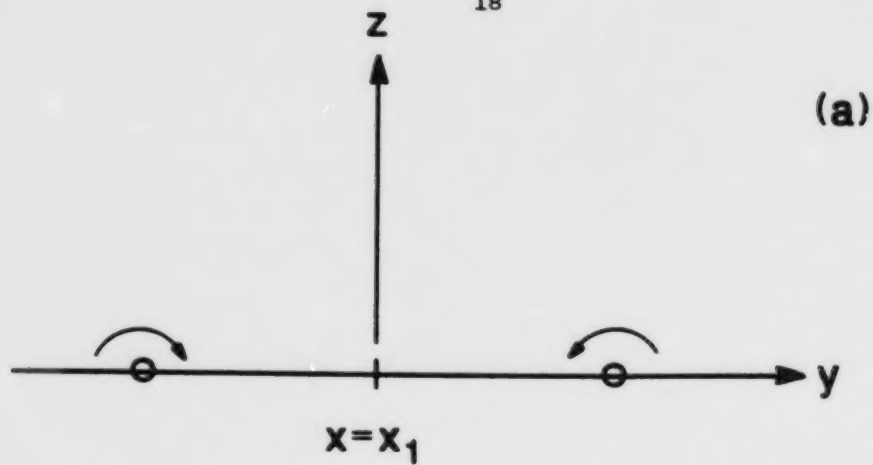


Figure 9. Fluid motion induced by vortices is indicated by direction of arrows. Ground effect is represented by image vortices.

the expression for G . The last two terms account for the image vortices shown in figure 9b generated by the presence of the ground. They induce the swirling motions shown by the arrows which tend to push the clumps of particulate outward as they near the ground.

Discretization

To actually solve the equations defining the problem, it is necessary to discretize the system spatially and integrate the resulting ordinary differential equations in the time like (downwind) direction. There are two crucial issues that must be addressed if the numerical simulation is to accurately approximate the continuous model. First, the velocities and their gradients must be analytically obtained from a discretized form of eqs. (8) and (9). Second, the evolution equations for ω and the coordinate gradients Q , R , S , and T (eqs. (5) and (7)) must be integrated in a mass-conserving scheme. Once these issues are addressed, the remainder of the calculation is similar to other vortex methods.

The key to resolving both issues is the recognition that conservation of mass implies

$$QT - RS = 1. \quad (10)$$

Since the left hand side of equation (10) is also the Jacobian of the transformation between Eulerian and Lagrangian coordinates, it implies that the integral expressing the solution for Ψ in eq. (9) has the same form in Lagrangian coordinates. It can be conceptually discretized in Lagrangian coordinates to $O(h^2)$ accuracy by replacing the integral by a sum of squares of side h and using the value of ω at the center of each square. To the same order accuracy, this can be done with circles of the same area. The crucial point now is to recognize that a small circle of radius r_0 in Lagrangian coordinates must be transformed into an ellipse in Eulerian coordinates whose principal semi-axes a , b are given by:

$$\begin{aligned} a^2 &= r_0^2 / (\mu + \lambda); \quad b^2 = r_0^2 / (\mu - \lambda) \\ \mu &= \frac{1}{2}(\alpha + \beta) \\ \lambda^2 &= \frac{1}{4}\{(\beta - \alpha)^2 + 4\gamma^2\} \\ \alpha &= R^2 + Q^2; \quad \beta = S^2 + T^2; \quad \gamma = QS + RT \end{aligned} \quad (11)$$

The ellipse is rotated with respect to the Eulerian coordinates by an angle θ obtained from:

$$\tan(2\theta) = 2\gamma / (\alpha - \beta) \quad (12)$$

These expressions exactly preserve area (and hence mass) if eq. (10) is satisfied. The solution for the stream function Ψ for an ellipse containing a uniform prescribed vorticity is well known [12]. Since it is expressed analytically it resolves the first major issue.

To resolve the second point note that eqs. (7), which allow Q, S, R , and T to be advanced in the downwind direction, imply eq. (10) for any set of

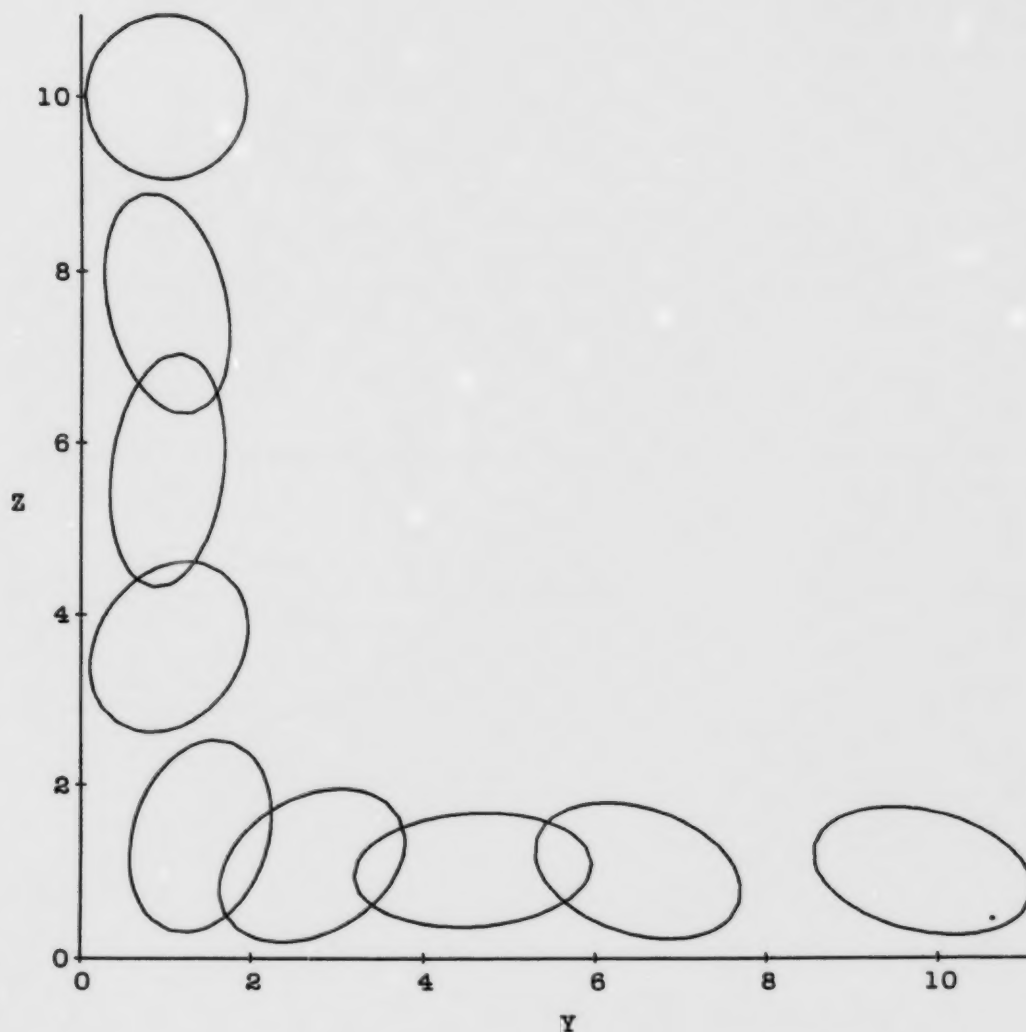


Figure 10. Evolution of right hand member of a vortex pair of constant vorticity as it approaches ground at $Z=0$. Left hand member is mirror image.

velocity gradients which conserve mass. If now, the velocity gradients are held fixed in time for the duration of a time step δ , then the equations can be analytically integrated. The resulting expressions, which will not be recorded here, exactly preserve eq. (10) for each vortex. Since the analytical results for S and T over the whole time interval δ are available, they can be integrated once more in eq. (5) to obtain an updated value of ω . This value is at least second order accurate in δ . The whole process then is a patchwork of locally exact continuous solutions to the inviscid equations, which, taken together, constitute the discretized problem. The further steps, which involve advecting the ellipses under the influence of the composite velocity field, is common to any vortex method. The evolution of the right hand member of a descending vortex pair is shown in figure 10. The vorticity of each blob is held fixed for illustrative purposes, but the shape and trajectory evolve according to the equations derived above. The shapes are shown at different instants of time. Note that they rotate as well as deform.

The whole approach is similar in spirit to that employed by Ghoniem [13] as a part of his Transport Element Method. Ghoniem retains circular vortices but adds additional ones as needed if the fluid elements become too elongated. Teng [14] has worked with elliptical vortices in simulating constant density viscous flows past a flat plate. However, his ellipses were rigid and non-rotating, which is not locally consistent with the flow kinematics. The present approach attempts to make maximum use of the analytical information available and build it into the computation. It is of necessity more specialized than that of Ghoniem, but hopefully will prove a more faithful representation of the equations it is intended to solve.

FUTURE STUDIES

Preparations are being made for large-scale tests of oilspill burning. This research program is preparing means to make measurements at the large-scale tests that can be compared to existing laboratory data.

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BUBBLE GROUP BEHAVIOUR UNDER MICROGRAVITY CONDITIONS APPLIED TO SUBSEA BLOWOUT PLUME MODELLING

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ABSTRACT

The frequently observed intermittent behaviour of subsea blowout plumes and the mechanism of gas release from the wellhead during a blowout have led the authors to believe that these structures should be modelled as a series of bubble groups. A fundamental study of bubble group behaviour has therefore been undertaken as the starting point for such a model. This paper discusses a set of experiments which were carried out on a NASA KC-135 aircraft in order to determine the effect which gravity has on bubble group behaviour.

INTRODUCTION

The events of recent months have drawn attention to the environmental damage which can be caused by oil spilled in Arctic waters. In the event of an uncontrolled subsea blowout, the buoyancy of the gas would cause hydrocarbons and entrained seawater to rise to the ocean surface, where the vertical motion would deflect radially outwards from the bubble plume with little loss in momentum. This would generate a shallow, fast-moving layer which could transport the oil in the plume a considerable distance from the blowout point. The large area and small thickness of the slick make containment and collection at the ocean surface difficult.

The ideal solution would be containment of the hydrocarbons before the bubble plume has a chance to fully develop. The design of such a device requires a knowledge of the complex fluid flow phenomena near the wellhead, since it is this behaviour which affects the overall development of the plume. Should the blowout be impossible to contain or cap, a number of predictive models have already been proposed for bubble plumes based on the assumption of steady flow in the established portion of the plume [1]. However, the mechanism of gas release at the wellhead [2], which involves the shattering of large bubbles into many smaller bubbles, and the frequently observed intermittent behaviour of bubble plumes have led these investigators to believe that a plume model based on the intermittent release of bubble groups rather than a continuous flow of gas would be more appropriate.

For the development of such a model, a fundamental knowledge of the dynamics of bubble groups is necessary. A laboratory investigation into the various physical variables which affect bubble group development has therefore been undertaken. Dimensional analysis shows that any parameter which may be used to describe the behaviour of these structures should be a function of the following dimensionless groups:

$$\text{Parameter} = f \left[\frac{V_A^{1/3}}{H}, \frac{\rho_l (V_A g)^{1/2}}{\mu}, \frac{\rho_l V_A^{2/3} g}{\sigma} \right]$$

The first of these groups is a length ratio, the second is a form of liquid

Reynolds number and the third is a Weber number. Examination of these dimensionless groups shows that the variables which could affect bubble group behaviour are the injected gas volume, the height of the water above the orifice, surface tension and gravitational acceleration. These were chosen as the dependent variables in the laboratory work. To be perfectly correct, the gravitational acceleration term should be accompanied by a ratio of the density difference ($\rho_g - \rho_l$) to the liquid density ρ_l since these variables always act in conjunction. However, the negligible density of the gas phase in comparison with the liquid phase means that this ratio is approximately equal to unity and can be neglected.

Although a number of analytical and experimental investigations of bubble plumes appear in the literature [1], all of the published data is for air-water systems. In order to provide a basis for comparison between bubble groups and bubble plumes, water was chosen as the continuous phase and air as the dispersed phase for these experiments. The density difference and the liquid density and viscosity are thus constant for the purposes of this work.

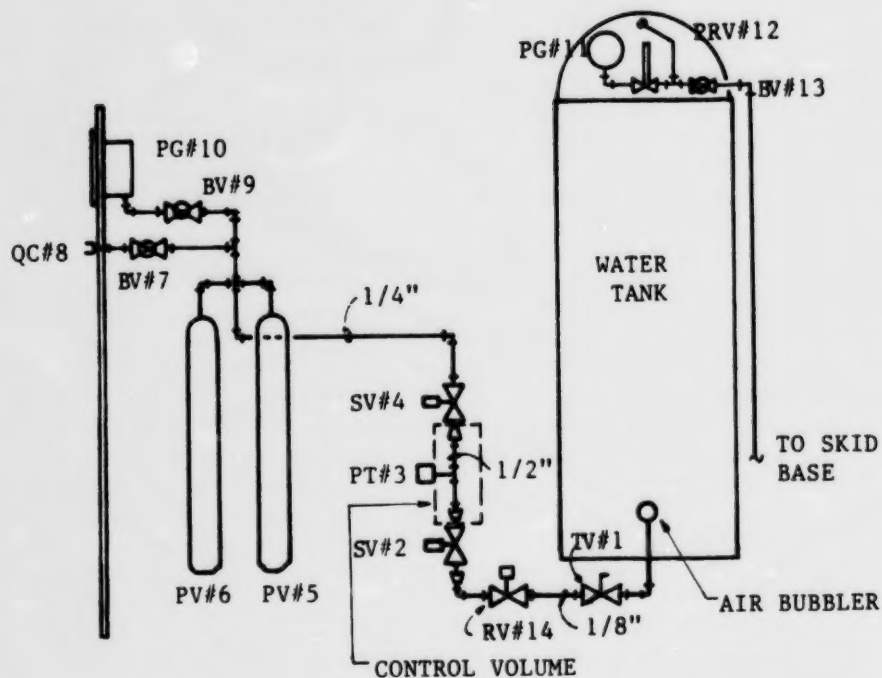
The majority of the experimental work, which examined the effects of varying water height, injected air volume and surface tension, was carried out in a laboratory at the University of Calgary under Earth-normal gravity. The results of these investigations have been reviewed in other publications [3,4]. This paper discusses a similar series of experiments performed on a NASA KC-135 aircraft in order to determine the effect which gravity has on bubble group behaviour.

KC-135 EXPERIMENTS

The NASA KC-135 is a modified Boeing 707 transport turbojet which provides a "weightless" environment similar to that of space. The KC-135 is flown in a series of parabolic arcs to provide 20 to 25 second periods of near zero-gravity (better than 10^{-2} g). Each parabolic maneuver is accompanied by a pull-up and pull-out of between 1.8 and 2.0 g. The University of Calgary bubble group study was one of thirteen Canadian experiments accepted by the Space Division of the National Research Council to take part in their March, 1989 series of flights at the Johnson Space Centre in Houston, Texas.

The bubble group tests were carried out using two equipment skids designed to bolt to the floor of the KC-135. The first skid held the small water tank used in the 1.0 g laboratory experiments, which had been modified to meet NASA structural testing requirements. A sealed plenum was added to the top of the tank to prevent the release of water into the aircraft cabin, and to keep the air pressure at the top of the tank at a relatively constant value. Next to the tank was the pressurized air system used to release the bubble groups into the water and the control volume pressure readout. The second skid carried the VCR and video camera which recorded the bubble group data, and the remote controls for the air injection system.

Figure 1 is a schematic of the pressurized air system attached to the water tank. Before takeoff, the air storage cylinders were pressurized and the air in the plenum was brought to ambient pressure. During the flight, the control volume was filled by remotely activating solenoid valve SV#4, and the pressure recorded using the remote readout from the absolute pressure transducer PT#3. Bubble groups were released by opening solenoid valve SV#2. The volume of air in each bubble group was calculated using the pressure difference in the control volume before and after the injection. The control volume was then filled for the next run.



LEGEND

<u>LABEL</u>	<u>DESCRIPTION</u>
BV	Ball Valve
PG	Pressure Gauge
PRV	Pressure Reducing Valve
PT	Pressure Transducer
PV	Pressure Vessel
QC	Quick Connect
RV	Regulating Valve
SV	Solenoid Valve
TV	Toggle Valve

FIGURE 1 - SCHEMATIC OF PRESSURIZED AIR SYSTEM

Scale:

N.T.S.

A total of 106 parabolas were allotted to this experiment: 40 on the first flight day; 46 on the second; and 20 on the third day of flights. The extra six parabolas flown on the second day included three at Moon gravity ($1/6 g$) and three at Mars gravity ($1/3 g$). Bubble groups were released under microgravity conditions and also during the $1.8 g$ pullout. Data were recorded for 76 of the parabolic maneuvers; the remaining 30 were lost due to problems with the VCR.

Due to the limited storage area in the pressurized air system, the pressure in the control volume decreased slightly with each run and the pressure in the plenum increased. Because of this, each bubble group's volume was lower than that of its predecessor. The difference was small enough, however, that the volume could be considered constant for comparison purposes within a short range. Enough valid data were gathered to provide information for three air volumes and three g -levels at the one water height. It was not possible to determine group radius and velocity values from the zero- g runs, but bubble group behaviour under microgravity conditions will be described in the following section.

In order to determine the exact value of the gravitational acceleration at the time each group was released, the output from the control volume pressure transducer was recorded on computer by Dr. Bjarni Tryggvason, the Canadian astronaut responsible for monitoring the linear and angular accelerations of the KC-135 during the flights. Although these acceleration traces had not been received from NRC Space Division at the time of writing this paper, the investigators are confident that their comparisons are realistic as the bubble groups were not released until a g -level had been fully established.

It was originally intended to examine the effects of varying surface tension as well as injected air volume in the KC-135 experiments. However, this test was deleted because the alcohol used as a surfactant in the laboratory experiments would have provided a safety hazard onboard the aircraft. As well, it would have etched the surface of the Lexan tank walls, therefore ultimately preventing video recording of the bubble group behaviour.

Several occurrences during the flights may have affected the quality of the results. At the beginning of each $0 g$ portion of a parabola, there was usually a short period of negative g . This caused the air in the plenum on top of the tank to form a large bubble in the water. Sometimes, if the negative g was strong enough, this large bubble would travel all the way to the bottom of the tank and break up the smaller bubble group. Lateral accelerations in the aircraft also caused some migration of the bubble groups away from the injector axis, which is where the radius and velocity measurements were calculated. During each period of Moon and Mars gravity, more than one bubble group was sequentially released in order to gather as much data as possible for these g -levels. The water in the tank was therefore not completely quiescent between runs, which may have affected these measurements to a small degree.

EXPERIMENTAL OBSERVATIONS

The previous laboratory experiments have demonstrated that two-phase bubble groups exhibit the characteristic behaviour of single-phase thermals in the formative stages of their development. "Thermal" is a meteorological term which denotes the turbulent motion arising from a suddenly released source of buoyancy into an infinite medium. The buoyancy of atmospheric thermals is due

to a density difference between the thermal and the surrounding air, resulting from a difference in temperatures. Because atmospheric thermals are lighter than their surroundings they rise vertically, entraining the surrounding air as they progress by convective mixing across the density interface. The rate of spread of a single-phase thermal is constant due to the similar interior circulation pattern throughout its existence. Bubble groups, however, have two stages of growth: an initial circulating period where the bubbles move with the liquid; and a second phase where the bubbles rise vertically, leaving the circulating liquid behind.

The transition between the two stages is characterized by the release of a vortex ring from the main body of the bubble group. The vortex remains at the top of the moving fluid in the wake of the bubbles, and as it rises it expands linearly and decelerates. On the average, the vertical velocity of the bubble group is two to three times that of the vortex. The water in the wake of the bubble group continues to rise even after the bubbles have passed above the free surface.

Figure 2, which is a plot of the radius of the bubble group's widest point versus height above the top of the airstone for one injection volume and water height and three values of gravitational acceleration, illustrates the two stages of growth identified for bubble groups. The first stage, which at 1.0 g typically extends 100-150 mm above the airstone, is characterized by high entrainment and velocity levels near the injector. All of the laboratory bubble groups, regardless of injected volume and water height, had a constant entrainment coefficient α (proportionality constant relating radius to height) of approximately 0.2 in this initial growth period. This is comparable to single-phase values, which range from 0.1 to 0.35, with an average of about 0.25 [5]. In the latter part of its development, the bubble group radius also grows linearly with height, but with an α value an order of magnitude smaller than in the first stage.

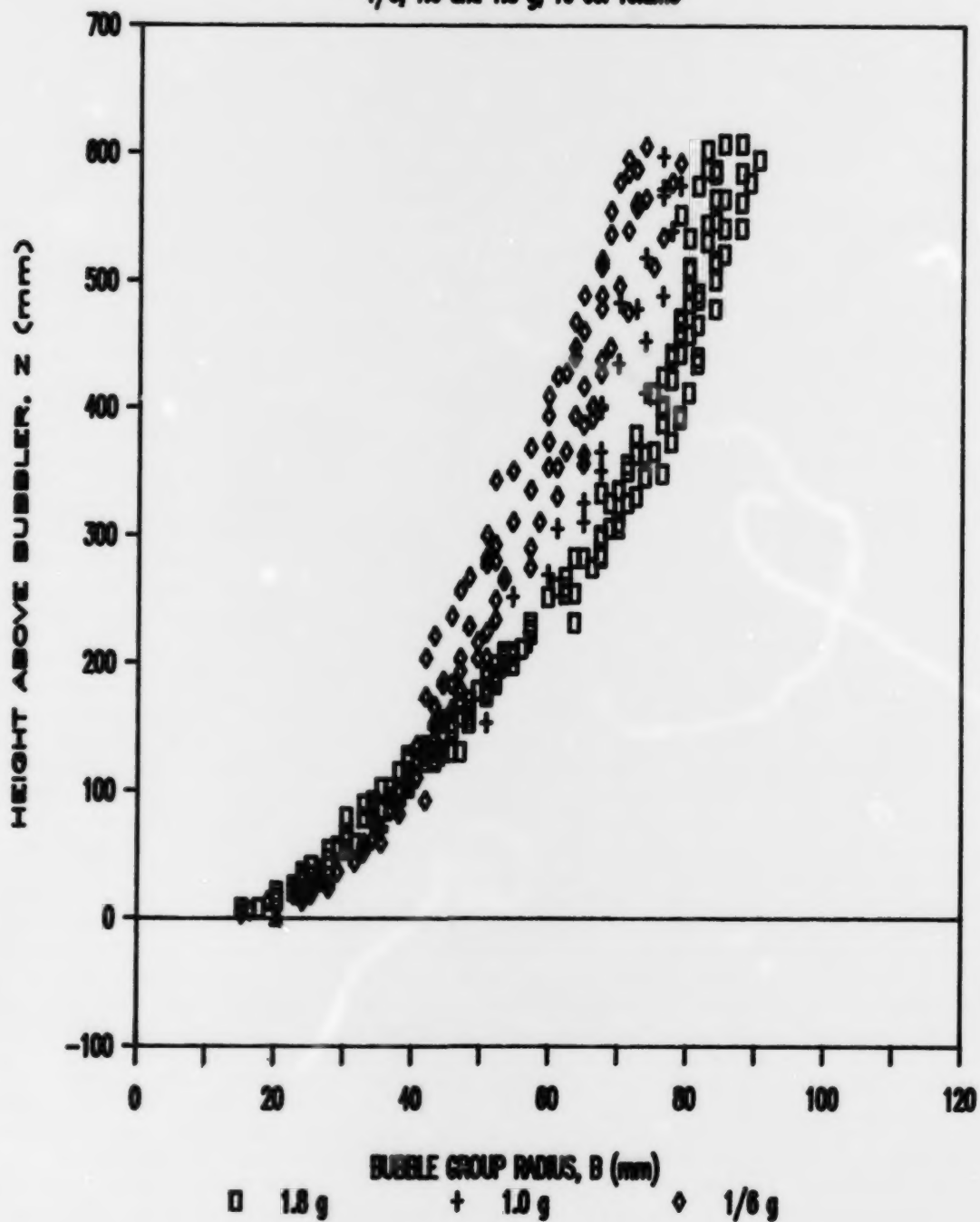
The most significant feature illustrated in Figure 2, however, is that the higher the gravity level is, the higher in the tank the transition from the "thermal" stage to the vertical rise stage occurs. The flight videos also confirm that the vortex ring release takes place further away from the airstone with larger gravitational accelerations. This can be explained by the increased buoyancy of the bubble group for an equivalent air volume as the g-level becomes stronger. The resultant momentum increase is transferred to the water, enabling the liquid to stay with the bubbles a further distance. Also, the size of the bubbles released at the injector was smaller with an increase in g due to the shorter time period it took for the bubbles to form. Previous surface tension experiments have shown that smaller bubbles tend to follow the liquid flow for a much longer period of time than large bubbles. With a decrease in surface tension, however, the entrainment coefficient increased in the second stage of growth. Figure 2 illustrates a decrease in α with increase in gravitational acceleration after the transition point.

It should be noted, however, that the time frame for the occurrence of the vortex release was the same for all levels of gravitational acceleration (approximately one second), even though the distance from the airstone was further. The velocity of the bubble groups was also affected by gravity; increasing as the g-level increased. This effect cannot be attributed to the decrease in bubble size, as all of the bubble diameters observed in the experiments should have had terminal velocities in a similar range (Haberman and Morton [6]).

Figure 3 illustrates bubble group radius plotted against height above the

FIGURE 2 - RADIUS CHANGE WITH HEIGHT

1/6, 1.0 and 1.8 g, 10 cc. Volume



airstone for the same level of gravitational acceleration (1.8 g) and three different injection volumes. It shows that the bubble group radius in the second stage of growth increases with injection volume. This is very similar to the results observed in the 1.0 g laboratory experiments.

As was mentioned before, it was not possible to draw any quantitative conclusions from the bubble groups released under microgravity conditions. The primary reason for this was that at 0 g, the bubbles would form on the airstone but would not detach until they were forced to by a small difference in the acceleration level of the plane. The bubbles formed in microgravity were significantly larger than those formed under any sort of gravity. When the bubble group did detach from the airstone, no transfer of momentum to the water was ever evidenced by the release of a vortex ring. However, if a bubble group was released just before a period of 0 g, a vortex ring would form and continue to rise through the bubble group, which would remain stationary due to its lack of buoyancy in microgravity.

DISCUSSION

The experimental results to date have shown that the entrainment coefficient is constant in the initial phase of bubble group development, but is proportional to the injected air volume in the second stage of growth. This conclusion is valid at any of the levels of gravitational acceleration investigated except for 0 g. Since α is a local and not a global variable in bubble plumes (i.e. it varies with the distance from the origin), it is not surprising to note that the entrainment coefficient of approximately 0.2 seen for bubble groups in their formative stage is the same order of magnitude as that at the source of a bubble plume [7].

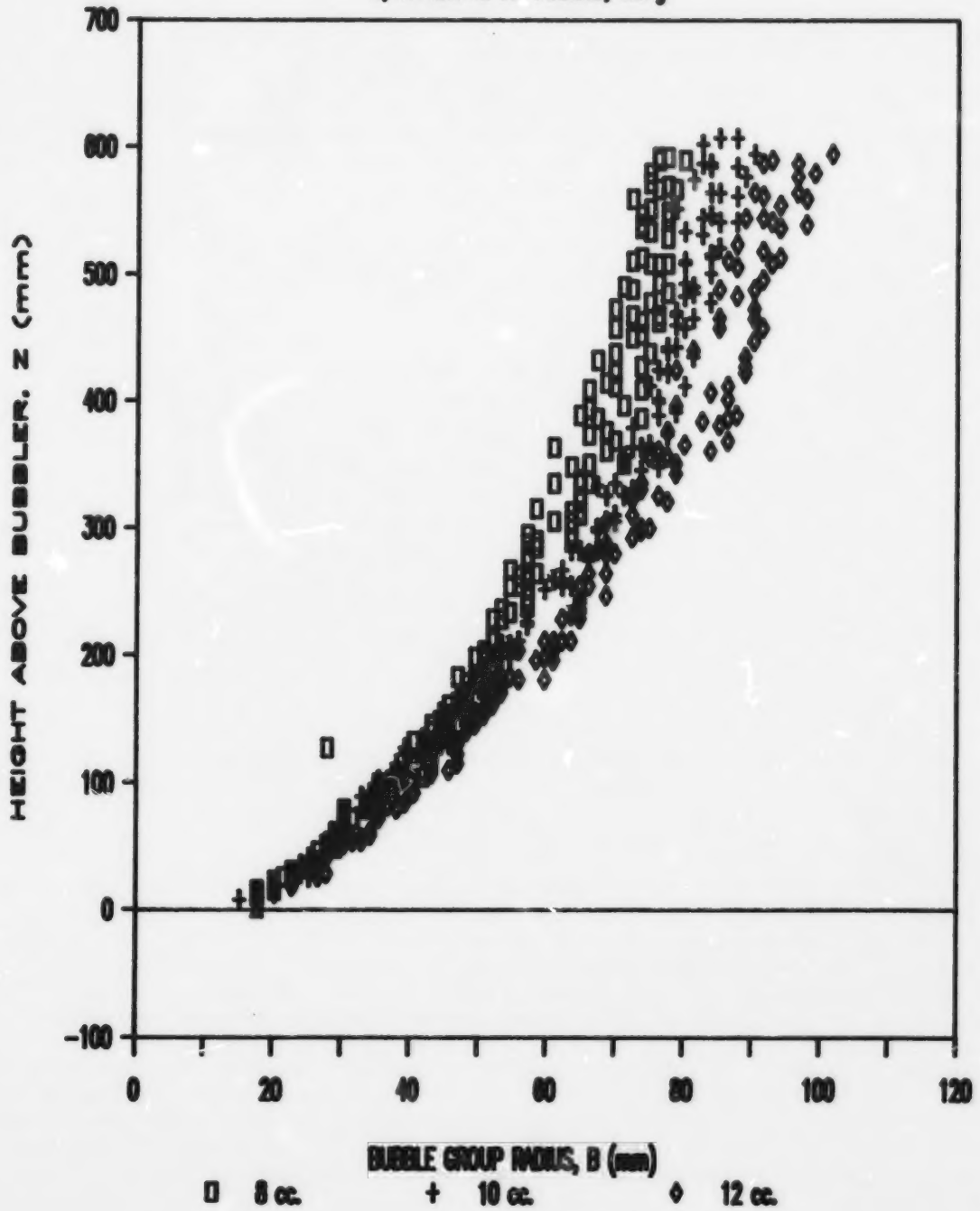
Higher gravitational accelerations also lengthened the distance before transition occurred from the circulating to the vertical rise stage and the detachment of the vortex ring from the main body of the bubbles, although the time was the same for all g-levels. This agrees with the overall increase in bubble group velocity with gravity which was observed in the KC-135 experiments.

Increasing the g-level had the further effect of decreasing the size of bubbles released at the airstone. Smaller bubbles are better able to follow the circulating liquid flow due to a lower slip velocity, although the bubble sizes observed in the experiments should not have had an appreciable difference in terminal velocity. Thus, it is assumed that the longer distance to transition is due to the increased momentum imparted to the bubble group from an increase in buoyancy, rather than to the smaller bubble diameter.

In the laboratory experiments, it was seen that reducing the surface tension of the water by the addition of small amounts of alcohol also had the result of decreasing the size of the bubbles formed at the airstone. The addition of a minute amount of this surfactant (0.05% by weight) had a drastic effect on reducing the size of some of the bubbles, while most of them remained at their original diameter. Further increases in alcohol concentration increased the number of tiny bubbles formed until eventually the entire group was composed of very small bubbles. After this point, no further reduction in bubble diameter could be obtained. In comparison, increasing gravitational acceleration gradually reduced the initial size of each bubble in the group. Also, gravity increase tended to reduce the entrainment coefficient in the second stage, while lowering the surface tension resulted in an increase in α .

FIGURE 3 - RADIUS CHANGE WITH HEIGHT

8, 10 and 12 cc. Volumes, 1.8 g



A simple two-phase thermal model which will describe both the gas and liquid behaviour is currently under investigation. Functional relationships relating the behaviour of the gas and liquid phases before and after separation are also being developed. Although it had previously been assumed that the Weber number would be the significant dimensionless group in these functional relationships [3], it now appears that it will only prove useful in determining how long the initial circulating stage will last. The length ratio may also be discounted because the 1.0 g experiments have shown that water height has little effect on the overall bubble group development in the scale of these experiments. Currently, the Reynolds number appears to be the most promising dimensionless group on which to base any correlations.

ACKNOWLEDGEMENTS

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NOMENCLATURE

B	bubble group radius at the widest point	Z	vertical coordinate
g	gravitational acceleration	α	entrainment coefficient
H	source depth	ρ_g	density of gas phase
V_A	injected gas volume at atmospheric conditions	ρ_l	density of liquid phase
		μ	viscosity
		σ	surface tension

A STUDY OF THE LONG-TERM WEATHERING OF SUBMERGED AND OVERWASHED OIL

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SUMMARY

Progress in an on-going study is described of the long-term weathering phenomena which are experienced by heavy crude oils and residual fuels when present on a sea surface and subject to overwashing, evaporation, dissolution and photolysis. Experiments were designed and conducted to measure the increase in density of four oils (two heavy Californian crude oils, Cold Lake bitumen and a bunker fuel) as they were subjected to these weather processes. A novel experimental system for making these density measurements was devised. Experimental results were obtained and analysed. A mathematical model was developed and fitted to the data. It is concluded that the primary causes of increased density are evaporation of the more volatile and less dense components of the oil and incorporation of denser-than-water mineral matter into the oil. The effect of dissolution on density is negligible. It is hoped that the results of the mathematical model will assist in the elucidation of the conditions under which heavy oils become subject to permanent sinking in the marine environment.

Recommendations are made for future work, especially the development of protocols for determining the susceptibility of oils to density increase by evaporation and dissolution and the development of expressions describing the extent of overwashing and episodic sinking.

INTRODUCTION

The Phenomenon of Sinking

Conventional oils and petroleum products when spilled in the marine environment almost invariably float on the water surface and are subject to a number of processes including evaporation,

dissolution and photolysis, formation of oil-in-water emulsions and water-in-oil emulsions, these processes being collectively termed "weathering". A considerable number of studies has been undertaken of the rates of these processes, and mathematical models have been developed describing and predicting these rates, and the effects these processes have on oil properties (Mackay and McAuliffe, 1988). Generally, the oil becomes denser because of evaporation of the less dense, volatile hydrocarbons but the density rarely increases to that of water i.e. 1000 kg/m^3 in freshwater or approximately 1024 kg/m^3 in marine water. It is of concern, however, that certain heavy crude oils and residual products such as Bunker C which have densities exceeding 900 kg/m^3 could increase in density to the extent that they become denser than water and become subject to sinking. This could lead to a significant environmental impact because the sensitive and often economically valuable benthic environment could become contaminated by masses of sunken oil. The implications for lobster or shell fisheries are obvious. It is therefore prudent to ascertain if these oils can become denser than seawater, and if so, what conditions will cause this phenomenon.

Previous studies by Wilson et al. (1986), Clark et al. (1987), Ross (1987) and Buist and Potter (1987) have shown that the sinking phenomenon is not simply one of negative buoyancy. When an oil mass is weathered and the density approaches that of water it sinks more deeply into the water and becomes subject to appreciable overwashing as the result of wave and current actions in the near-surface region. The oil may in fact spend an appreciable fraction of its history underwater being conveyed in near-surface currents by large eddies. It may thus be invisible to observers at the sea surface, or to remote sensing systems. Several incidents have occurred in which there has been anecdotal evidence that oil masses have submerged, only to reappear at distant locations on the water surface.

Five processes are believed to contribute to an increase in oil density.

1. Evaporation

Evaporation tends to remove from the oil the more volatile hydrocarbons which also tend to be the less dense chemical species. Accordingly, the residue will show an increase in density.

2. Dissolution

Oil components are subject to dissolution, particularly as a result of overwashing by wave action. Again the more soluble hydrocarbons will preferentially dissolve. The preferential dissolution of the less dense lower molecular weight species, and especially the lower molecular weight aromatics may result in an increase in oil density.

3. Photolysis

Photolytic processes can result in polymerization to form denser, higher molecular weight species. Photolysis may also cause the formation of free radicals which are susceptible to oxidation resulting in the formation of denser oxygenated species as peroxy and hydroxyl radicals, alcohols, ketones, carboxylic acids and aldehydes.

4. Attachment of foreign matter

The oil mass comes into contact with mineral matter such as diatomaceous material and biota which may become attached to the oil, or become incorporated into it, resulting in an increase in density. This process has been observed and reported by Wong et al. (1984) and may be responsible for oil sinking especially in areas of high suspended solids content, for example in relatively shallow near-shore waters, estuaries or during storms. One situation in which this process is very important occurs when viscous oil masses drift into the breaking wave region close to sandy shores. The oil drops, which may range from a few millimetres to a few centimetres in diameter may pick up sand particles, thus becoming denser. Eventually they may become incorporated into the beach, or if the tide is receding, they may drift out to sea and become partially or totally submerged, or sink to the bottom. Evidence was obtained from the "Nestucca" barge spill off the BC coast in late 1988 to the effect that collected oil contained an appreciable sand content and thus had been subject to this process (Fingas-personal communication, 1989).

5. Water uptake

Finally, it is likely that most oils incorporate water both by dissolution and formation of water-in-oil emulsions thus causing an increase in oil density. In some cases, in which the

oils contain emulsion-stabilizing species, water volumetric contents as high 80 to 90% have been observed.

The Experimental Approach

A laboratory research program was designed to measure density increases over periods of approximately 20 days, of oils exposed to various weathering regimes including evaporation, dissolution, contact with solid materials and microbiota and photolysis. It was decided to use four oils of relatively high density and high viscosity. These were Cold Lake Bitumen (CLB), California Crude Oil API 11 (C11), Bunker C Fuel Oil (BC) and California Crude Oil API 15 (C15). These oils were subjected to physical-chemical property determinations and analysis by gas chromatography. A program of exploratory research was then undertaken to devise a system in which oils could be exposed to various weathering regimes and the density increases monitored using a relatively non-disturbing technique. This proved to be difficult, but after some trial and error an exposure measurement system was devised which it is believed gives as good results as is possible with the present state of knowledge and resources. A mathematical model is being developed to express or "fit" and correlate the density increases in a quantitative manner. The experimental results obtained are described briefly in this paper. It is hoped that ultimately this study will yield an equation for density variation with time which contains a minimum number of adjustable parameters which describes satisfactorily the observed experimental data. With appropriate caution the equation may have the potential to predict density increases of oils in marine environmental conditions.

EXPERIMENTAL

The four oils tested supplied by Environment Canada and the US Minerals Management Service are listed along with selected physical-chemical properties in Table 1. This table contains data kindly provided by M. Bobra. Table 2 gives information on the composition of these oils obtained by open column liquid chromatography under the defined conditions. Gas chromatograms are shown for the fresh oils in Figures 1 to 4. The oils were contacted with double distilled water and salt water consisting of 32 parts per thousand sodium chloride (NaCl) and the water soluble fraction subjected to analysis. California Crude 15 showed the presence of appreciable concentrations of lower aromatics having a total water solubility of approximately 26 mg/L in freshwater and 15 mg/L in salt water. Since the average solubility of these hydrocarbons is some

Table 1. Properties of Crude Oils and Residual Fuels

Property	California Crude No. 15.0	Bunker C Fuel Oil	California Crude No. 11.0	Cold Lake bitumen temp. (°C)	reference	
API Gravity	13.2	12.3	10.3	9.8	20	Environment Canada (EC)
Density (kg/m ³)	990.7	994.1	996.8	1007.5	0	EC
	983.2	990.4	994.2	1004.9	5	EC
	980.2	986.7	991.5	1002.3	10	EC
	977.0	983.0	988.2	1000.2	15	EC
	973.5	978.8	985.2	996.8	20	EC
	968.1	971.2	977.9	985.1	22 ± 2	this work
	970.2	974.9	982.4	994.3	25	EC
	967.2	971.8	979.6	991.6	30	EC
Viscosity (cp)	6.4E3	1.4E6	2.2E5	>3.0E6	0	EC
	3.1E4	4.8E4	3.4E4	2.4E5	10	EC
Solubility (mg/L) d.d.H2O	25.7	4.23	11.3	0.26	22 ± 2	this work
	salt H2O*	14.7	1.95	9.74	0.13	22 ± 2

*3.0 wt% NaCl in salt water

Table 2. Hydrocarbon Analysis by Open Column Chromatography

	weight %			
composition	California Crude API 15.0	Bunker C Fuel Oil	California Crude API 11.0	Cold Lake bitumen
saturation	13.7	31.3	13.7	16.6
aromatics	36.4	45.7	29.8	39.2
asphaltenes	25.8	10.8	24.8	19.3
NSO compounds	24.1	12.2	31.7	24.9

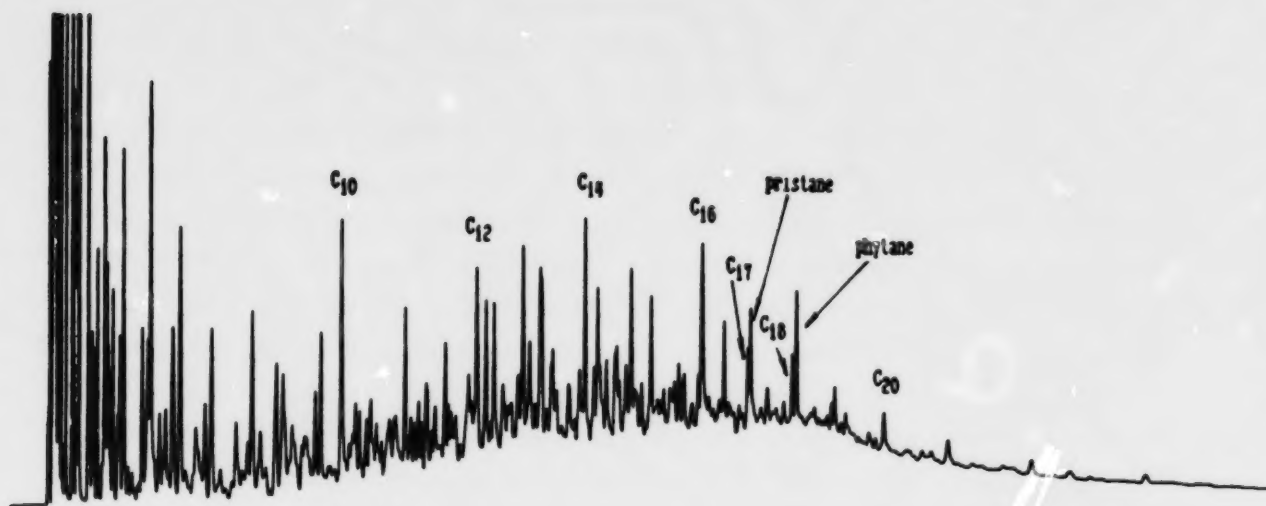


Figure 1 Gas Chromatogram of fresh California Crude Oil (API 15).

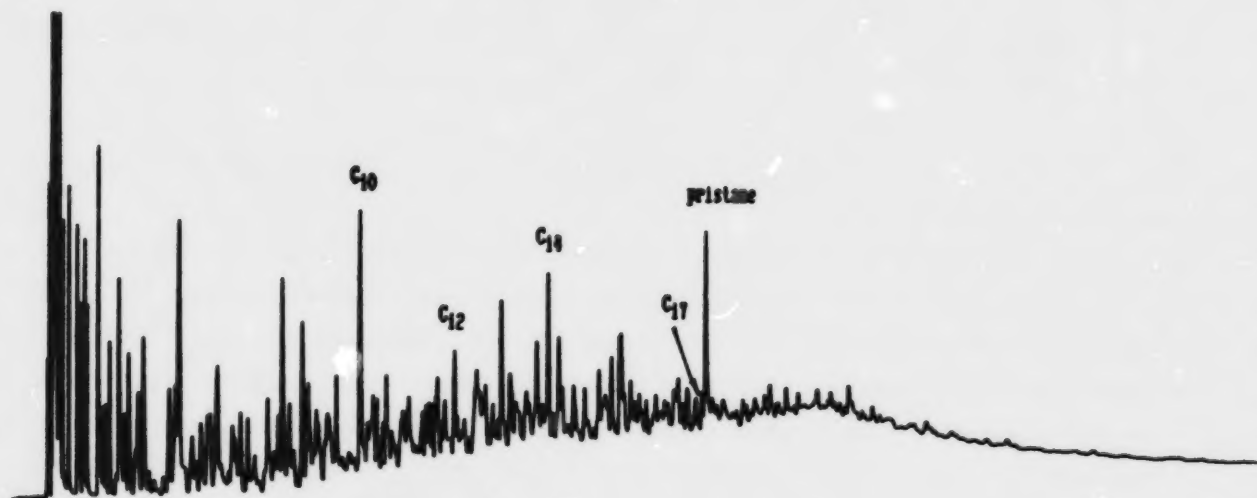


Figure 2 Gas Chromatogram of fresh California Crude Oil (API 11).

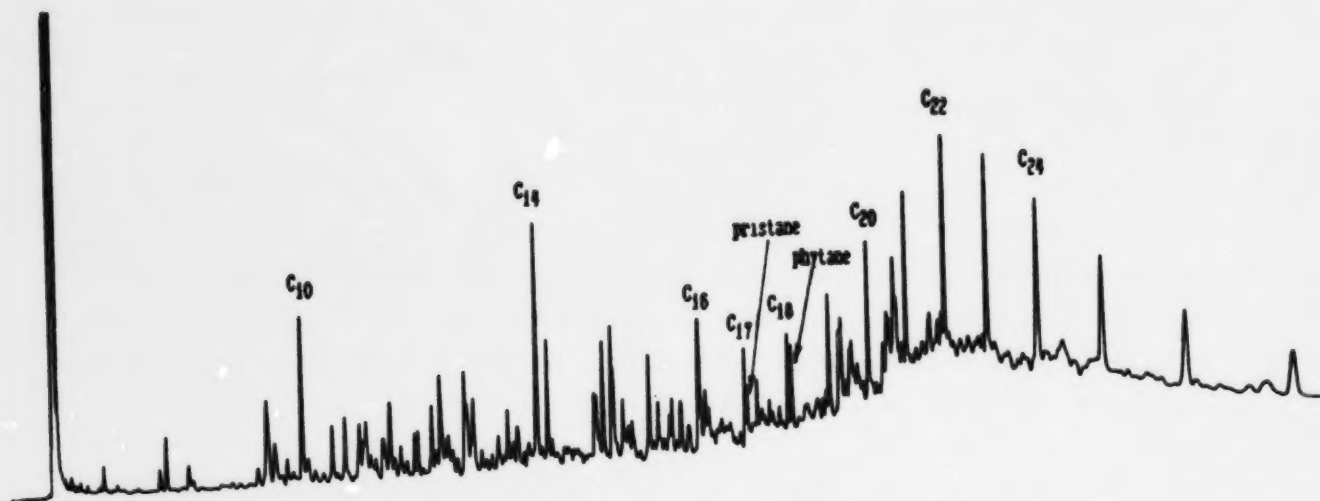


Figure 3 Gas Chromatogram of fresh Bunker C Fuel Oil.

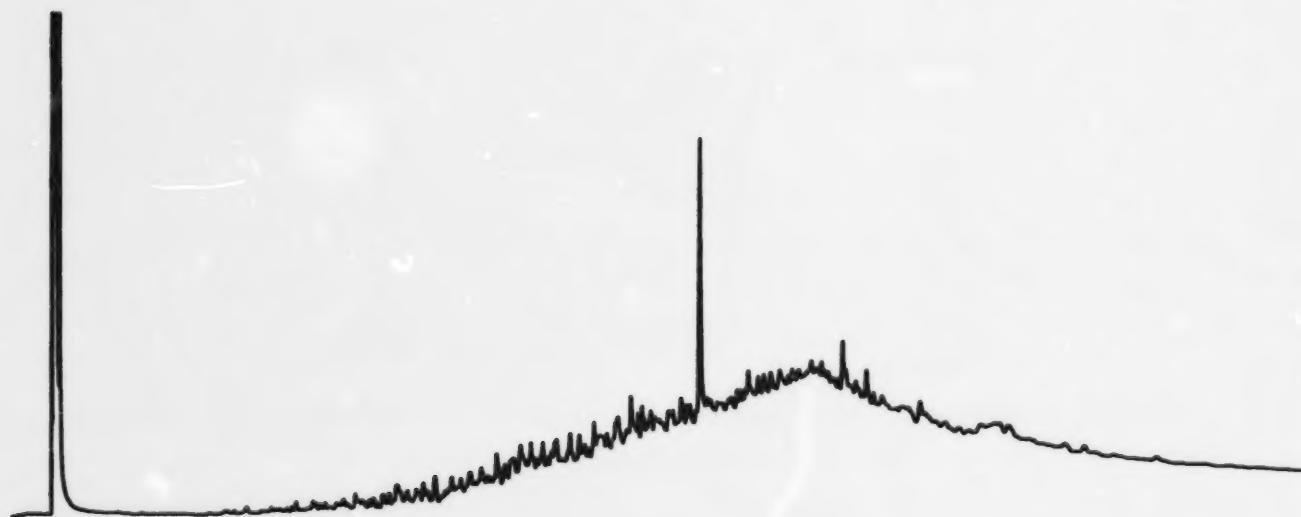


Figure 4 Gas Chromatogram of fresh Cold Lake Bitumen.

400 mg/L, it appears that this oil contains a mole fraction of these fairly soluble hydrocarbons amounting to 25/400 or 0.06 or approximately 6%. California Crude 11 had approximately half of this quantity. The Bunker C Fuel Oil had a very low concentration of aromatics presumably as a result of extensive distillation. Cold Lake Bitumen had only negligible contents of lower aromatics.

Density Determination

The system eventually adopted for exposure and density determination is illustrated in Figure 5. Disks were obtained of polyester mesh of diameter 6 cm made from PeCap polyester manufactured Tetko Inc. This mesh has an opening of 0.5 mm and a filament diameter of 0.3 mm. A number of mesh sizes and thread diameters were tested, however, this combination was found to be most suitable in that the oil was well retained by the mesh with a minimum of "dripping". Plastic mesh is preferable to metallic mesh because of its lower density.

The approach used to determine densities was basically the Archimedean principle of weighing the oil mass in air and in water, the difference being the buoyancy induced by displacement of the volume of water. Corrections were introduced for the presence of the mesh. The equation used (in units of kg and m³) was:

$$\text{Density of oil } D_o = \text{Mass of oil } M_o / \text{Volume of oil } V_o$$

where

$$M_o = M_T - M_M$$

where M_T is the mass of oil plus mesh in air and M_M is the mass of the mesh,

and

$$V_o = V_T - V_M$$

where V_T is the total volume of oil plus mesh and is calculated from

$$V_T = (M_T - M_{TS}) / D_w$$

where M_{TS} is the apparent mass or weight of the submerged oil plus mesh and D_w is the density of the water. $(M_T - M_{TS})$ is thus the buoyancy induced by the water.

V_M is the volume of the mesh which was determined by weighing the mesh in air and water.

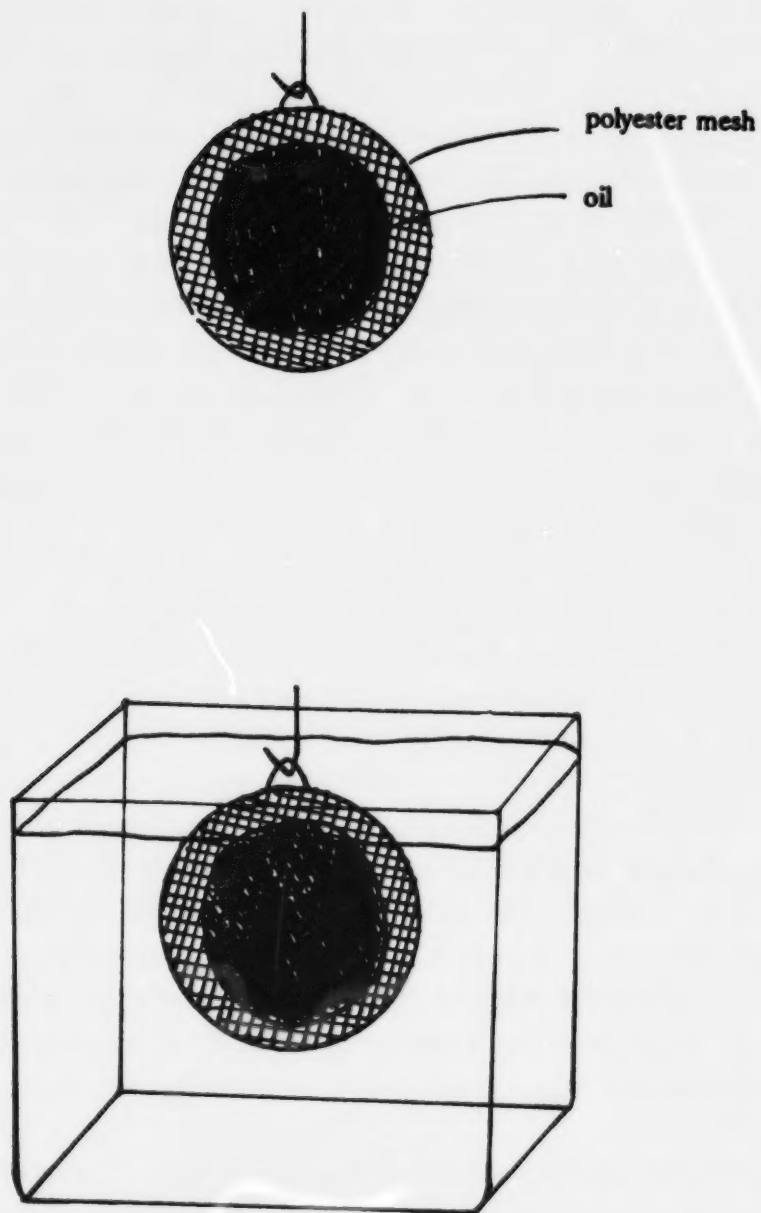


Figure 5 Diagram of experiment system in which oil-coated mesh disks are weighed in air and in water. The disk diameter is 6 cm.

Care was taken to remove all air bubbles from the oil and mesh during weighing in water and to minimize surface tension effects on the suspending filament. In the early stages of the work considerable effort was devoted to improving technique, accuracy and precision.

Usually, 0.5 to 1.0 g of oil was coated on to six mesh disks of 60 mm diameter with heat-sealed edges. This gave a reproducible and controlled area/volume ratio.

A Hewlett-Packard GC model 5700A equipped with a flame-ionization detector was used to analyze fresh and weathered samples of oil obtained from the oil weathering experiments. The column was 0.05 cm ID x 50 m long glass capillary column. The operating conditions were: the initial oven temperature was 50°C for 8 minutes and the oven temperature was programmed to 250°C at a rate of 5°C/min. The injection sample has a volume of 0.5 μ L with a split ratio of 50:1, and peak areas recorded with a Shimadzu Chromatopac C-R1A integrator using the area normalization method.

For the column chromatographic separation approximately 1.5 g of oil was diluted in 100 mL of n-pentane. The mixture was filtered through a pre-weighed filter to remove the asphaltene content. The filter was dried in a heating compartment for 24 hours before being weighed again to determine the percentage weight of asphaltene.

The de-asphalted oil was separated into three fractions: saturates, aromatics and polar compounds using the procedure described by Cook and Westlake (1976). A dual-phase column packed with 1:1 ratio of silica gel and alumina was used. The silica gel (28-200 mesh) and alumina (type F-20, 80-200 mesh) were supplied by Sigma Chemical Co. The order of elution was as follows: saturates with pentane, aromatics with benzene, and then soluble polar compounds with a 1:1 mixture of benzene-methanol. The collected fractions were concentrated and later weighed to obtain the percentage composition of each fraction in the crude oils.

The following weathering experiments were conducted on the four crude oils:

- evaporation in the fumehood in the dark,
- evaporation in the fumehood with photolytic exposure,
- dissolution in a continuous flow of distilled water,
- dissolution in salt water,
- biodegradation,

- contact with suspended inorganic particles, and
- dissolution with photolytic exposure.

Evaporation

From initial tests, it was found that only a small fraction of oil (up to 20%) was retained on the disc when it was held stationary in air; therefore, a rotating device was devised which rotated (at a rate of 1.0 rpm) the oil-covered discs continuously between a horizontal and a vertical position. However, there was a small possibility of oil dripping off the discs during the first few days. The apparatus was placed in a fumehood that had a fairly high air flow. Two runs of the evaporation experiment were performed for 3 to 4 weeks with one at 19-20°C and the other at 22-24°C. Density measurements were taken after, 6, 24, 48, and 72 hours from the initial exposure for the second run because the greatest changes in density occur during the initial evaporation period.

The remaining experiments were conducted at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Photolysis in Air

The source for photolysis was two fluorescent UVA-340 40-watt lamps which were mounted on standard light fixtures in the fumehood. The 48 inch fluorescent tubes were obtained from the Q-Panel Company. The lamp's emission was in the UV-A region with a small amount of UV-B. This is believed to be a satisfactory simulation of sunlight in the critical short wavelength UV region in the range 365 nm to 295 nm.

Oil samples on the discs were again circulated vertically on a rotating device.

Dissolution

Stainless steel hooks attached on to glass rods were used to hang oil-covered mesh disks vertically into a tank containing 27 L of distilled water. The disks were spaced apart at a distance of 2.5 cm. A constant daily flowrate of water was maintained with inflow of fresh water supplied by an overhead cylindrical tank. The disks were rotated 90° from the original position every two days for the first two weeks to prevent the oil from flowing off the disks and creating a slick on the water surface. Approximately 1.0 g of oil per disk was applied.

A second dissolution experiment used salt water instead of distilled water. Instant Ocean[®] (manufactured by Aquarium Systems) was used to provide the salt content which approximately simulates that found in sea water. Only 0.5 g of the oil was applied on each disc because of the high tendency for the oil to separate from the disk and float to the water surface. Half of the 7.5 L salt water was replaced weekly with a freshly-made solution of equal density.

Density measurements for both dissolution experiments were made weekly. However, before the densities of the oils could be determined, the oil-discs were dried on a rotating device in the fumehood. Inevitably this resulted in some dissolution.

Photolysis in Water

This apparatus was similar to the dissolution experiment except for the additional use of sunlight-simulation lamps. The UVA-340 lamps were angled such that more ultra-violet light was received by one side of the glass tank. After each weekly measurement, the disks from the two different sides were manually interchanges so that each oil had the same light exposure.

Contact with Inorganic Particles

In the initial experiments purified bentonite powder (supplied by Fisher Scientific Co.) of 0.1 wt% in distilled water was used to expose the crude oils to suspended mineral matter. This mixture had to be continuously stirred at a moderate speed to produce a uniform suspension of particles throughout the 7.5-L tank. High stirring speeds caused the oil-coated disks to collide with each other.

Before the oil densities can be determined, the discs were initially immersed in distilled water in an attempt to displace the bentonite particles from the exposed mesh openings. The oil covered disks were then dried on the rotating device for about 40 minutes.

After these initial experiments a more comprehensive series of experiments was undertaken exposing the oils to a series of mineral materials, including:

- Pottery clay purchased from a local hobby shop
- Riverbed clay obtained from a river near Whitevale, Ontario
- Kaolinite obtained from the Geology Department, University of Toronto

- Diatomaceous earth (Fisher)
- Soapstone, i.e. talc, obtained by grinding a piece of soapstone obtained at a hobby shop for carving purposes

Soapstone was used because it is reputed to be very "hydrophobic" and may thus be unusually susceptible to oil attachment.

MATHEMATICAL MODEL

The general aim of the mathematical model is to provide a quantitative description of the change in density of the oil as a function of exposures such as evaporation, dissolution, contact with solid materials and photolysis. This provides a method by which the experimental data may be converted into parameter values which can be used to correlate the data and possibly predict the effect of exposure to several density-increasing regimes. No previous models exist describing these density increases, thus the development described here is novel and undoubtedly will be the subject of improvement as a result of scrutiny and testing against future experimental data. The approach used should thus be regarded as exploratory in nature.

In the interest of brevity only the general nature of the final correlating equations is presented here. The forthcoming project report will contain a more detailed derivation and justification.

Evaporation

The oil is treated as consisting of three components, a volatile fraction (1), a less volatile fraction (2) and an involatile residue (R). It can be shown that such a mixture will increase in density D according to an equation of the form shown below in which D_R is the residue density and E_1 and E_2 are the products of the volume fraction of components 1 and 2 and the density difference $(D_R - D_1)$ and $(D_R - D_2)$. Two rate constants k_1 and k_2 are introduced.

$$D = D_R - E_1 \exp(-k_{E1}t) - E_2 \exp(-k_{E2}t)$$

This can be rearranged to give an expression for the density increase from that of the original oil density $(D_R - E_1 - E_2)$ namely,

$$\Delta D_E = E_1(1 - \exp(-k_{E1}t)) + E_2(1 - \exp(-k_{E2}t))$$

Further, rather than report k_1 and k_2 as reciprocal times (e.g. 0.01 h^{-1}) it is more meaningful to report them as $1/T_1$ and $1/T_2$ where T_1 and T_2 are characteristic times, e.g. 100 hours.

Dissolution

A similar analysis can be conducted for dissolution yielding an equation for density increase as a function of dissolution which is identical in structure to that for evaporation, but only one component is needed

$$D = D_R - F_1 \exp(-k_{D1}t)$$

or

$$\Delta D_D = F_1(1 - \exp(-k_{D1}t))$$

If the components which evaporate are not those which dissolve then the equations for evaporation and dissolution could be added and evaporating and dissolving components could be identified separately. In reality this is unlikely to apply because the components which dissolve will tend to be those of lower molecular weight which probably are also subject to evaporation, i.e. E_1 and F_1 are equivalent. It is therefore probably more reliable to add the rate constants for evaporation and dissolution and apply them to the same component thus giving an equation of the form shown below for two components

$$D = D_R - E_1 \exp(-(k_{E1} + k_{D1})t) - E_2 \exp(-k_{E2}t)$$

or

$$\Delta D_{DE} = E_1(1 - \exp(-(k_{E1} + k_{D1})t)) + E_2(1 - \exp(-k_{E2}t))$$

Photolysis

For photolysis we postulate that some of the residual oil experiences a density increase thus the overall density of the oil increases according to an equation of the form.

$$D = D_R(1 + Gt)$$

where G is a fitted constant. An alternative and possibly preferable expression is

$$D = D_R + D_p(1 - \exp(-k_p t)) = D_R + \Delta D_p$$

where ΔD_p is a density increase attributable to photolysis and k_p is a rate constant.

In practice it is likely that some part of the component 1 will also be subject to photolysis. However, it is probably impossible to discriminate this from the residue using experimental data thus we prefer to assume that photolysis only applies to the residual material. Some justification of this approach is obtained by noting that photolysis occurs at the surface of the oil which is most severely depleted by evaporation and dissolution.

Attachment of Foreign Matter

When foreign matter such as clay, microorganisms or diatomaceous matter becomes attached to the oil the bulk density of the oil will increase according to the equation

$$D = ZD_F + (1 - Z)D_O$$

where Z is the volume fraction of foreign matter of density D_F and D_O is the oil density. This can be rearranged to the more convenient form below by expressing density as a function of the difference between the solid density and the oil density and the density.

$$D = D_O + Z(D_F - D_O)$$

thus

$$\Delta D_F = Z(D_F - D_O)$$

As is discussed later there appears to be a non linear density increase with an initial rapid uptake followed by a slower uptake. This may be due to a viscosity increase or the coverage of the surface by mineral matter. A convenient correlating expression is

$$Z = Z_F(1 - \exp(-k_M t))$$

where Z_F is the final value of Z and k_M is a rate constant.

Overall Density Equation

Combining the expressions for evaporation dissolution, photolysis and attachment of foreign matter, the density of an oil mass is postulated to be described by the equation given below which contains adjustable parameters for the various processes. Examination of the magnitude of the parameters will show which of the processes are important and the rates of the density increase which can be expected

$$D = D_o + \Delta D_{DE} + \Delta D_p + \Delta D_F$$

The key problem is to obtain values of the parameters E_1 , E_2 (alternatively F_1 and F_2), k_{E1} , k_{E2} , G , Z_F and k_M . An expression is being included to allow for separate exposure times to dissolution evaporation and photolysis to be included depending on the overwashed state of the oil. If this can be accomplished it will result in a relatively simple and easily understandable expression for oil density increase.

Evaporation vs. Dissolution

Finally, a theoretical analysis was undertaken to explore the relative importance of evaporation and dissolution as removal processes contributing to density increases. It was concluded that only those hydrocarbons with vapour pressures exceeding approximately 0.04 Pa (approximately that of hexadecane) will evaporation be significant in about a week. Similarly only hydrocarbons (or other chemicals) with solubilities exceeding 1 g/m³ (approximately that of phenanthrene) will dissolve appreciably.

Hydrocarbons which have vapor pressures below 10⁻² Pa or solubilities below 1 g/m³ will be substantially retained by the oil and are unable to migrate into air or water because of the very low concentrations which they can establish in these receiving phases.

The alkanes to about C₁₆, the monoaromatics, the naphthalenes, the three membered PAHs and polar "hydrocarbons" containing O, N or S atoms are thus candidates for loss by evaporation or dissolution. The others are probably destined to remain in the oil. A consequence of this analysis is that it may often be fruitless to test the oil phase for evidence of loss of these chemicals, rather they should be sought in the "receiving" phases of air or water, i.e. the water solubility or

partial pressure of these chemicals should be measured as indicators of potential for migration from oil and thus for causing density increases.

RESULTS

Magnitude of Density Increases for Sinking

The data in Table 1 suggest that to reach a density of 1024 kg/m³ the oils must increase in density by the following approximate amounts at 10°C and 22°C.

	<u>10°C</u>	<u>22°C</u>
California 15	44	56 kg/m ³
California 11	32	53 kg/m ³
Bunker C	37	46 kg/m ³
C.L. Bitumen	22	29 kg/m ³

We are thus concerned with density increases in the range 20 to 60 kg/m³ which, if achieved by a single process or combination of processes could result in sinking, depending on the oil, the water and the prevailing temperature.

Evaporation

The first series of evaporation tests lasted for 21 days and showed that the oil density was increasing with time and served to confirm that the experimental method was valid. As a result of experience in this series, the number of replicates was increased from 3 to 5 and additional measurements of oil density were made early during the evaporation period because there was clearly a rapid increase in oil density during the first day. The second series of evaporation experiments yielded improved accuracy and a smaller standard deviation. The results for the four oils during this series are given in Figure 6. All oils showed a density increase during the first day presumably because of loss of volatile material. The Bunker C oil showed a relatively small increase presumably as a result of loss of volatile material during distillation. The Cold Lake

Figure 6. Evaporation

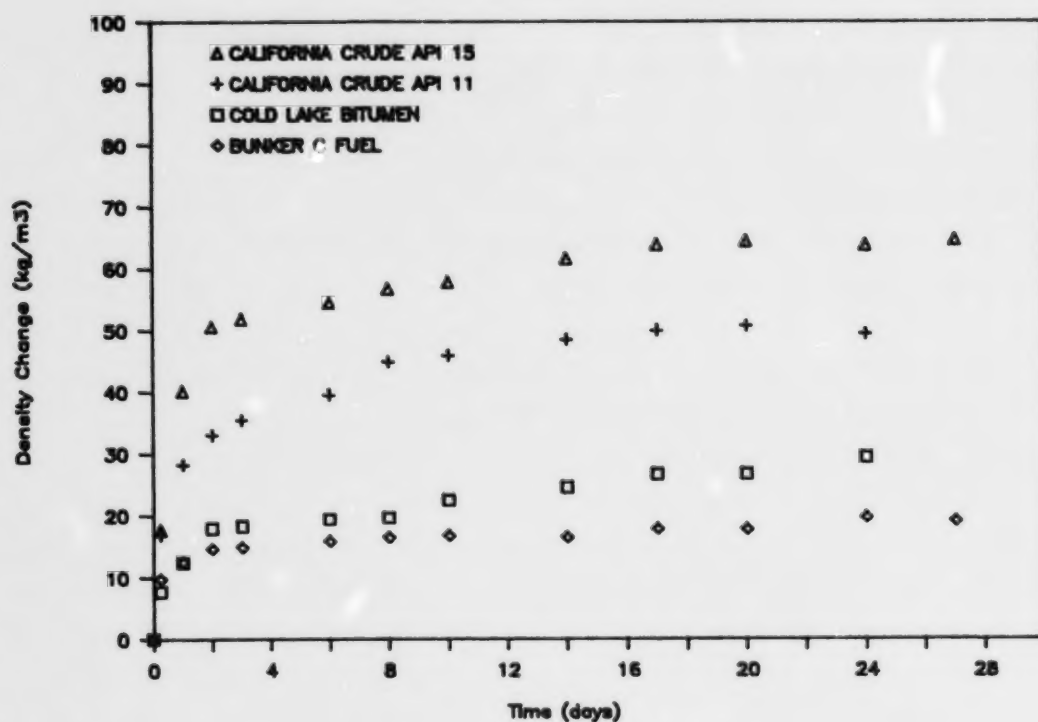
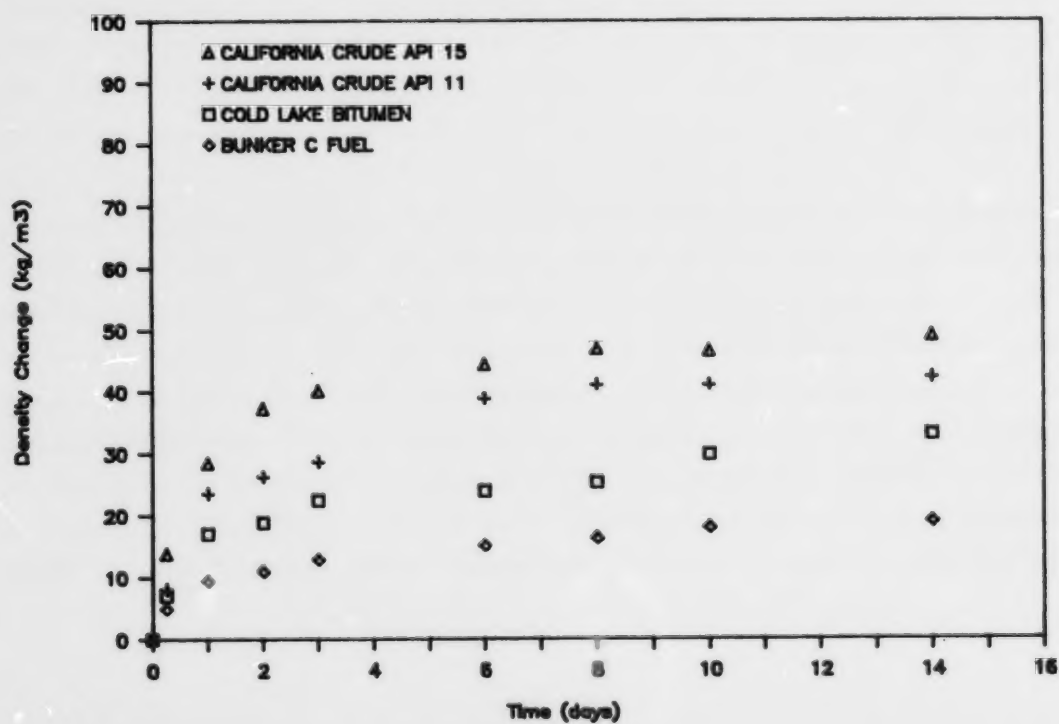


Figure 7. Photolysis in Air



bitumen also showed a fairly small increase in density. The two crude oils showed larger density increases and there was a continual increase in density after three or four days.

Examination of the curves suggest that accurate description of density increase require the incorporation of at least three components in the system, i.e. two components which evaporate and a residue. The first component appears to evaporate with a time constant of the order of two days or 50 hours and the second one with a time constant of approximately 16 days or 400 hours. The two crude oils, C11 and C15, eventually display densities approaching that of sea water.

The estimated parameter values are as shown below.

Evaporation Parameters (units of hours, kg and m³)

<u>Oil</u>	<u>E₁</u>	<u>k₁</u>	<u>E₂</u>	<u>k₂</u>	<u>D_R</u>
C11	38	1/50	15	1/400	1030
C15	51	"	13	"	1026
CLB	20	"	10	"	1014
BC	16	"	4	"	989

A note of caution is appropriate when interpreting of these results. The experimental technique is believed to be valid as a means of detecting density increases. The technique suffers from appreciable error in determining absolute densities because of the errors introduced in weighing and subtracting mesh masses and volumes. Occasionally a small amount of oil would float from the mesh surface thus confounding the density determination. It is possible that water dissolved in the oil thus affecting its weight in air, but not its weight in water. A compromise had to be made between prolonged drying with excessive evaporation and short drying with risk of retained water. Emphasis should be placed on the trends in relative density, not on absolute density.

Comparison of these parameter values suggests that the two crude oils are very susceptible to sinking, the C.L. Bitumen less so and the Bunker C is unlikely to sink by evaporation alone.

Evaporation Plus Photolysis

The effect of photolysis was generally to cause an increase in density beyond that of the evaporated oils, suggesting that photolysis either enhances evaporation (possibly by increasing the surface temperature of the oil) or results in formation of denser oil species. It was of course impossible to study photolysis in air in the absence of evaporation thus the approach taken was to calculate the increase in density of the photolyzed oil attributable to photolysis beyond that which occurred for the second evaporation experiment and attribute that incremental increase in density to photolytic processes. For example, for CLB and CB that increase corresponds to a density increment of about 5 kg/m^3 at 14 days or 336 hours. For C11 and C15 oils, the increase in densities attributable to photolysis was judged to be within the range of experimental error and no definite conclusion can be reached that photolysis causes an additional increase in oil density.

Fitting the data to the model suggests that the following values can be used.

Photolysis Parameters

<u>Oil</u>	<u>G (h⁻¹)</u>
C11	0
C15	0
CLB	1.5×10^{-5}
BC	1.5×10^{-5}

Dissolution

Experiments were run in parallel using fresh deionized distilled water and using salt water. The oil was not exposed to light except during the density measurements and the water was changed periodically to remove any components which had dissolved. The experiments ran for 42 days and showed a small increase in density. The variation in density was quite erratic during these experiments. This is partly due to some difficulties experienced experimentally in which there may have been loss of some of the oil from the meshes during the exposure. It appears that the crude

oils show a more significant increase in density probably as a result of the presence of more soluble lower molecular weight material. The density increase is in the range 24 to 31 kg/m³ for the crude oils and is about 15 kg/m³ for the fuel oils.

Fitting a one-dissolving component model gives the parameters below.

Dissolution Parameters

<u>Oil</u>	<u>Fresh Water</u>		<u>Salt Water</u>	
	<u>E_i</u>	<u>k</u>	<u>E_i</u>	<u>k</u>
C11	24	1/250	40	1/400
C15	31	1/250	70	1/400
CLB	15	1/250	20	1/400
BC	15	1/250	20	1/400

The most notable feature of the dissolution effect is its slowness (i.e. low k_i) relative to evaporation. Much of this density increase is believed to be due to evaporation.

The salt water results showed a greater increase in density especially for the crude oils. This was not expected and the reasons for it are unknown. It seems unlikely, but it is not impossible, that the oil picks up salt possibly through the formation of sodium salts of carboxylic and phenolic acids.

Attachment of Suspended Matter

Two series of experiments were taken investigating the attachment of suspended solid matter to the oils. The initial results for clay demonstrated a density increase of the order of 80 kg/m³. The second series of experiments yielded more accurate data and are discussed in more detail.

Figure 9 gives some typical density increases for selected mineral materials. In these tests the densities increased considerably, i.e. by 60 to 70 kg/m³ often reaching a value higher than that of seawater. There did not appear to be any strong influence of mineral type. The principal

Figure 8. Dissolution

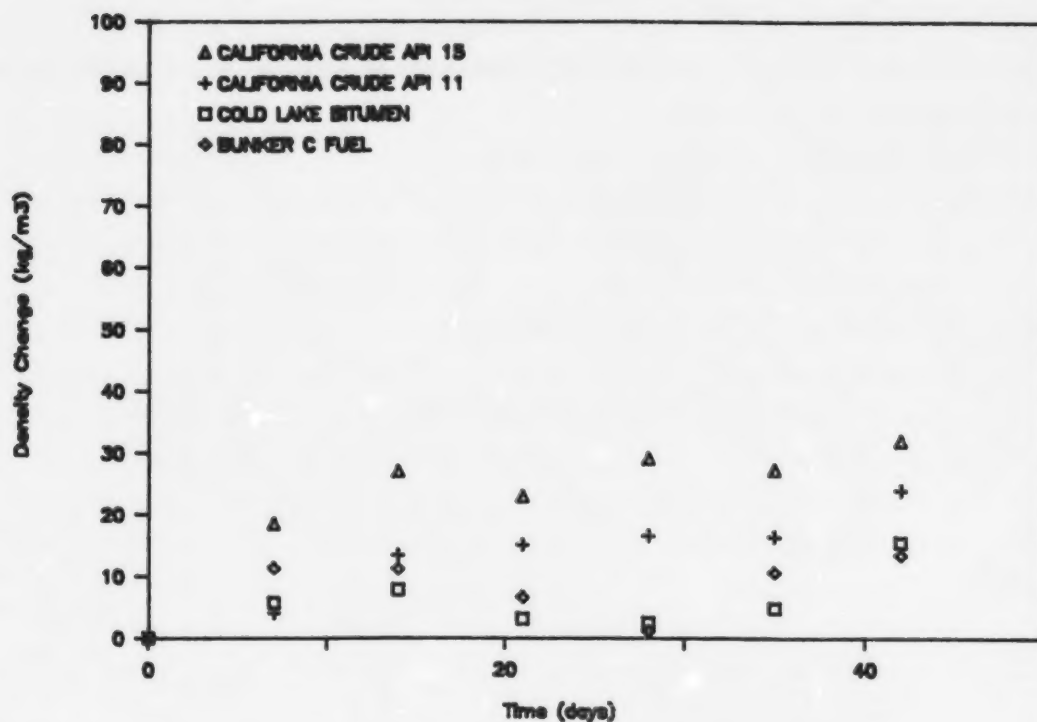


Figure 9. Incorporation of Particles

California Crude Oil API 15

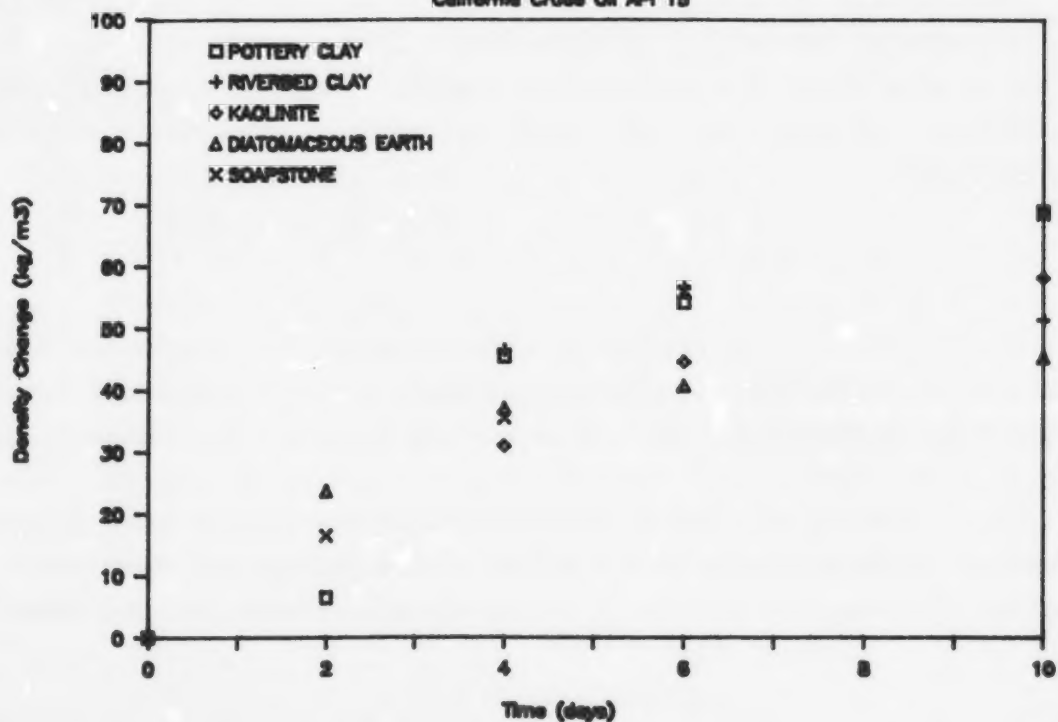
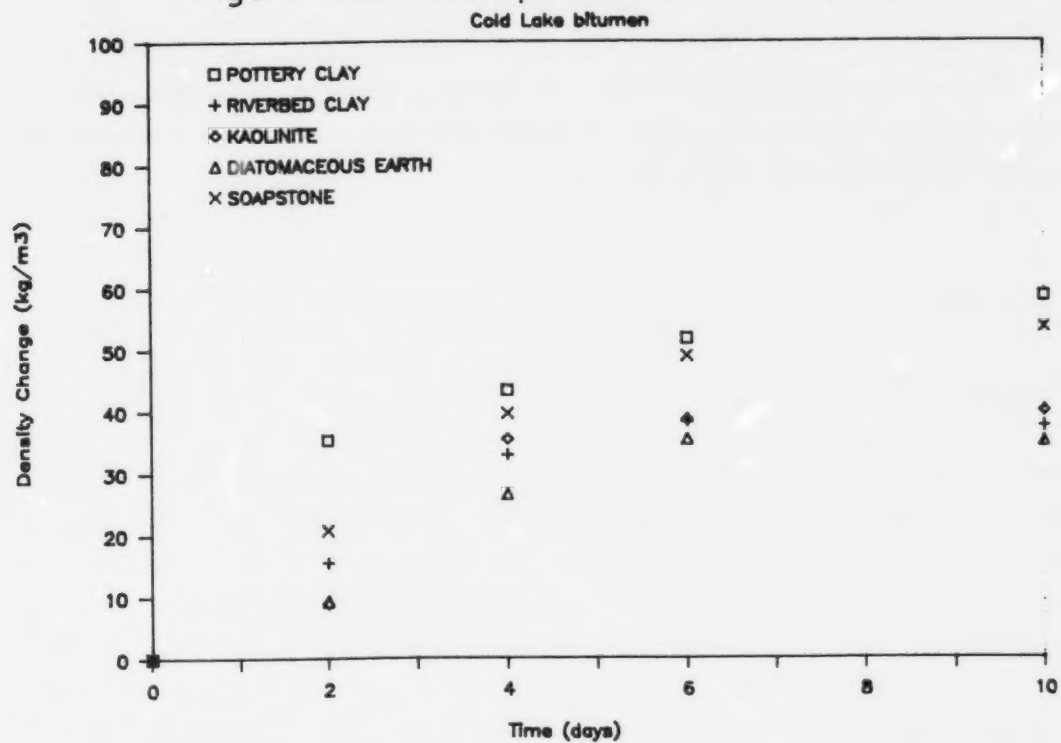


Figure 10. Incorporation of Particles



differences in behaviour between mineral types is attributable to differences in suspended solids contents. Some minerals (notably talc) proved to be difficult to maintain in suspension. Various approaches were tested in an attempt to standardize the solids concentration but this proved to be a formidable experimental task.

DISCUSSION

Susceptibility to Sinking

The results indicate that the primary causes of oil density increase are (in order of decreasing magnitude) evaporation, incorporation of solid material, photolysis and dissolution. Conditions can arise in which singly or in combination will cause the oil to achieve a density exceeding that of sea water. Evaporation is particularly important for the crude oils which still retain some of the lower molecular weight hydrocarbons which are fairly volatile.

It is clear that the magnitude of the density increases attributable to evaporation alone or incorporation of solid material alone are sufficient to cause sinking in exposure times relevant to oil spill countermeasures responses. Evaporation will be delayed by overwashing, but it is believed that many of the compounds may dissolve then evaporate, thus overwashing does not necessarily "shut off" evaporation. It is difficult to extrapolate these results to oceanic conditions because of uncertainties about overwashing and solids concentrations, but the results strongly suggest that sinking will occur for heavy crude oils.

Test Protocols

The results obtained in this study are of course specific to the oils which were tested. However, it is believed that for other oils similar parameter values probably apply. It is possible that the experimental approach used here could be used to establish a protocol for the assessment of likely submergence behavior of specific oils. The oil characteristic which is most variable is probably the density increase attributable to evaporation. This can be relatively readily ascertained by exposing a volume of oil to evaporation in a wind tunnel or fume hood under conditions of known wind speed and film thickness. The oil can then be collected and its density measured. Alternatively distillation under controlled temperature conditions could be used.

An attractive alternative would be to "strip" a sample of oil with a slow nitrogen stream at controlled temperature conditions and collect the evaporated hydrocarbons by cryogenic trapping. This would ascertain the content of hydrocarbon which has the potential to evaporate. A similar approach could be used for dissolved hydrocarbons using a "generator column", but trapping the dissolved hydrocarbons from the eluate, possibly in an extracting solvent. These techniques are potentially much more sensitive than looking for changes in composition of the source oil. It is recommended that these approaches be investigated.

Oceanic Phenomena

It is suspected that oil present in the near-surface region is subject to a "self-regulating" mechanism of density increase which will tend to cause it to adopt a density similar to that of the sea water. Evaporation will cause a density increase but only when the oil mass is exposed to air. There will also be active photolysis during daylight resulting in the formation of denser and more soluble hydrocarbons. There is often an accumulation of solid material at the turbulent water surface which will cause a further density increase. In total these processes will induce the oil to become denser, then sink. If the oil then passes into sea water of lower density it may be subject to sinking episodes and reach the benthic region. It is thus not surprising that heavy oils when exposed to marine environmental conditions often vanish from the sea surface for prolonged periods only to reappear in distant locations. Once submerged the oil may "stabilize" and be subject to only slight density changes.

The process of water in oil emulsion formation or "mousse" formation may also serve to increase the oil density, but in principle it is impossible for this process to cause the density to increase beyond that of sea water. Indeed for oils which have a density exceeding that of sea water, "mousse" formation will reduce the density.

A process which has not been considered in this work is that of dissolution of water in oil which may also cause a density increase approaching that of sea water. The magnitude of this effect is not known but it is believed to be slight.

A compelling case can be presented for subjecting fuel oils or crude oils which are high in density to a rigorous determination of submergence characteristics in order that on-scene response groups can be warned about the probability of the oil displaying submergence behavior.

Mathematical Modelling

This study has clarified the role of mathematical models as a tool for addressing these phenomena. It is suggested that two models are needed.

First is a density model in which appropriate oil property data are combined with information about exposure to evaporation, dissolution, photolysis and solid matter to yield estimated density differences between oil and water. The model presented earlier could form the basis of such a capability.

Second is a model describing the resulting behaviour of the oil. It is erroneous to suggest that oil floats until its density reaches that of seawater, then it sinks. In reality the submergence phenomena are more continuous. Buist and Potter (1987) have suggested correlations for oil "blob" size, the extent of overwashing and depth of penetration into the water column and the fraction of the oil which is submerged at any given time. Such a model gives the information required by on-scene response personnel.

Interestingly, it is likely that the two models are interdependent because evaporation rate is influenced by extent of submergence, thus in principle a combined model may be required.

CONCLUSIONS

It is believed that this exploratory study has elucidated the dominant processes causing oil density increase and will lead to a suggested protocol for a density increase assessment and a mathematical procedure for characterising these processes. This procedure could be incorporated with relatively little effort into existing oil spill models used for environmental assessment or for on-scene response purposes. Clearly further work is desirable to investigate the role of photolysis, better characterize evaporation process, study a variety of solid phases under various concentration conditions and develop appropriate mathematical models to aid those responsible for on-scene response.

ACKNOWLEDGEMENTS

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**STUDIES ON THE MECHANISM OF DISPERSANT ACTION:
WEATHERING AND SELECTION OF ALKANES**

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Introduction

Few studies have been conducted to investigate the changes in oil composition associated with chemical dispersion. Some workers have investigated the accelerated weathering or evaporation attributed to dispersant action, but did not attempt to quantify the effect. This study represents a first attempt to quantify these changes. Two specific phenomena were investigated; the accelerated weathering caused by dispersants, and secondly the change in the composition of the n-alkanes (the normal or straight-chain aliphatic compounds) which often constitute a large part of the oil's volume. These compounds are relatively easy to study by gas chromatography, being easy to identify and quantify.

The study of the compositional changes has relevance to numerous aspects of the dispersant question:

1. How do dispersants work? This question is very important because little is known about the mechanisms by which dispersants function. Most studies in the surfactant literature are related to micellization or detergency, two action mechanisms that have little relevance to oil spill dispersion. Understanding of dispersion mechanisms will greatly improve capability to improve dispersant effectiveness. Simply put, one cannot fix what one does not understand.

2. What causes effectiveness differences? The question of why similar oils with similar viscosities will sometimes display quite different dispersion, has plagued spill scientists for years. These variances were generally attributed to compositional differences, with no understanding of what the compositional differences were or how they affected dispersant action. The interaction of oil and dispersant composition is the most likely source of these differences.

3. Are there changes in oil composition which have relevance to environmental toxicity? Years of discussion have taken place over the question of whether chemically dispersed oil is more or less toxic than mechanically-dispersed oil. Most data show that the bulk toxicity of the two types of dispersions are about equal, although recent studies lean toward the finding that the chemically-dispersed oil is, in fact, less toxic. This finding would indicate that there are compositional changes caused by dispersants.

Dispersant-accelerated weathering (evaporation) has been

noted in the past by a number of workers. McAuliffe was the first to publish information on this topic.^{1,2,3} This phenomenon was further defined by McAuliffe in subsequent laboratory experiments where it was found that the C_2 to C_{10} hydrocarbons under a chemically-dispersed slick were of a lower concentration than under mechanically-dispersed slicks.⁴ McAuliffe subsequently reviewed a number of experiments, both field and laboratory, in which the accelerated weathering of C_2 to C_{10} hydrocarbons was measured.⁵ Wilson and co-workers conducted extensive tank experiments and noted a slightly-faster evaporation rate for chemically-treated oil.⁶ Anderson and co-workers noted major differences in the toxicity of mechanically and chemically-dispersed oil to shrimp.^{7,8} Further studies showed that the lower toxicity of chemically-dispersed oil was due to accelerated evaporation of toxic mono-aromatics.⁹ Bowler and co-workers conducted a number of experiments using a laboratory effectiveness apparatus and found that dispersants increased the evaporation rate of oil when comparing treated and untreated oil.¹⁰ Fingas and co-workers found similar accelerated weathering using dispersants on fuel in a model sewer system.^{11,12}

No studies dedicated to studying the chemical composition changes after the application of dispersant were found in the literature. Compositional changes in dispersed oil, were however noted by some workers while studying other facets of the dispersion process. Peake and Hodgson noted that water under an oil treated with an undecanoic acid surfactant was enriched in undecane, but attributed the effect to an anomaly which required further study.¹³ Wilson and co-workers noted that there was a compositional difference between the starting and dispersed oil, but suggested that the differences may be due to degradation.⁵ Shaw and Reidy found compositional changes but correlated these to mixing energy and not presence or absence of a dispersant.¹⁴

Experimental

Two forms of experiments were performed. First, evaporative loss was measured in laboratory dispersant effectiveness apparatus. Secondly, dispersant tests were performed in the swirling flask apparatus and the starting oil; surface oil, treated but undispersed; and the oil in the water column were analyzed using a gas chromatograph.

In the first set of experiments, three different apparatus were used. The swirling flask apparatus was operated according to published procedure.¹⁵ The MNS (Mackay-Nadeau-Steelman) or Mackay test was operated according to published procedure except that the oil-to-water ratio was maintained at 1:1200.¹⁶ The Warren Springs, Labofina or alternatively, the rolling flask test, was also operated according to published procedure except for the same oil-to-water ratio as above.¹⁷ The same oil-to-water ratio was maintained in all apparatus to eliminate this as a variable and also for the reason that lower ratios have been shown to effect results.¹⁸

All experiments were run in the same manner; oil was applied to the water surface, the apparatus energized in its regular

manner and after the run was completed, the surface oil was removed using 2.5 cm by 2.5 cm sorbent pads (SPC sorbent). These were in turn extracted using 30 mL methylene chloride. Concentrations were determined colorimetrically using a previously-prepared calibration curve. The calibration curves were prepared in analogous fashion to ensure that losses and sorbent efficiencies were accounted for. Results were repeatable to within 10%. The untreated crude oil was processed in the same manner as above to ensure that evaporation was compensated for. To account for accelerated weathering, experiments were done to measure the oil remaining on the surface and that in the water column. The amount lost to accelerated weathering was obtained by subtracting those amounts from the original amount added. The initial or untreated oil quantity was determined to be that amount left after processing in the apparatus without dispersants. This was done to ensure that losses, evaporation and inefficiencies were accounted for. The oil left on top after dispersion was determined using the sorbent procedure described above. Oil in the water column was determined by the published procedure for the apparatus and always involved extracting a portion of the oil and analyzing colorimetrically using a pre-determined standard curve. At least two runs were performed for every apparatus, oil and dispersant combination. If values were outside 15% experiments were repeated until the majority of values were within 15% of each other.

Five oils were used in both experiments. Their properties are given in Table 1. Mousse mix is a name given to a mixture of Bunker C and Alberta Sweet Mixed Blend (ASMB) and is frequently used in our laboratory for physical experiments. The name derives from the high tendency of that mixture to form mousse (water-in-oil emulsion).

Table 1 **Properties of the Oils Used In This Study**

Property	Condition	Oil				
		ADGO	ASMB	HIBERNIA	LAGO MEDIO	MOUSSE MIX
Density	15C	0.953	0.839	0.865	0.872	0.91
Viscosity	cSt at 15C	66	11	55	47	150
Interfacial Tension	mN/m 15C (oil/sea)	6.9	8.4	21	12	
Dispersant Effectiveness	% in Swirl-flask					
	Corexit 9527	61	38	8	7	15
	Enersperse	67	43	10	10	24

Gas chromatographic analysis was used in the second set of experiments to examine the composition of the starting oil, the surface oil and the oil dispersed into the water column. Methylene chloride extracts were performed as described above, effectiveness measured colorimetrically to ensure the consistency of results with those of previous experiments, and then a 0.5 microlitre portion of the extract was injected into a Hewlett-Packard 5890 chromatograph. The chromatographic conditions were as follows: initial temperature - 40°C, initial time - 5.0 minutes, temperature programming rate - 6.0°/min., final temperature - 300°C, final time - 30 min., and attenuation - 2. The column used was a SPB-1 and with helium as the carrier gas at a flow rate of 2.7 mL/min. The hydrogen flow rate for the FID detector was 30 mL/min and the air flow rate 240 mL/min.

A synthetic oil was made and run through the entire experiment to confirm that enrichment of certain n-alkanes as observed in the regular experiment was not a result of breakdown of the dispersant. No compounds other than those in the synthetic oil were evident in the gas chromatograph resulting from this test.

Weathering of Oil

The results of the experiments using laboratory effectiveness apparatus are summarized in Table 2. The values presented in this table are the amounts of oil unaccounted for after the oil on the surface and in the water column were computed, and thus represents the amount lost through evaporation since other losses were compensated for during the calibration procedure.

Table 2 EVAPORATION IN THREE APPARATUS

OIL	DISPERSANT	PERCENTAGE EVAPORATION IN APPARATUS			
		SWIRLING FLASK	LABOFINA	MNS	AVERAGE
ADGO	COREXIT	4	0	0	1
	ENERSPERSE	0	2	3	2
ASMB	COREXIT	25	31	2	19
	ENERSPERSE	11	25	7	14
MOUSSE MIX	COREXIT	15	6	2	8
	ENERSPERSE	9	8	14	10
HIBERNIA	COREXIT	30	18	10	19
	ENERSPERSE	25	4	14	14
LAGO MEDIO	COREXIT	4	3	12	6
	ENERSPERSE	30	12	2	15
					11

The accelerated weathering ranges from 0 to 30 % with an average of 11 %. These values should be taken in context with the error for each of the apparatus used; swirling flask 5%, Labofina 7%, and MNS 10%. All weathering values obtained were positive, thus indicating that despite the measurement error, dispersants always accelerate the weathering of the oil. The accelerated weathering is least in the MNS, as one might expect because the device operates with a high velocity stream of air and this would evaporate the untreated oil to a large extent. If the untreated oil is evaporated to a large extent the loss by accelerated weathering is small, because results are always compared to the weathering of this untreated oil after processing through the entire experiment. These results indicate that an average of 11% of the mass is removed over a short time period by the action of dispersants. Untreated oil would ultimately lose this mass by evaporation over a longer time depending on temperature and wind speed.

The accelerated weathering of oil was also examined in the second round of experiments. The swirling flask apparatus was used and untreated oil, surface oil and oil dispersed into the water column were examined by GC analysis. Examples of the gas chromatography data are displayed in Appendix Figures A1 to A11. The n-alkane peaks were calibrated between C_9 and C_{30} and relative amounts compared using the values from the GC integrator. A computer program was used to analyze the relative amounts of n-alkanes and then draw comparisons between compositions in the three fractions. The results of this analysis are presented in Tables A1 to A4 of the Appendix. Caution should be exercised in using these data, because a number of assumptions were made in the calculation. First, the individual peaks were not calibrated to the quantity of the compound; it was assumed that all the n-alkane compounds yield the same response on the GC detector. This is a relatively safe assumption under normal circumstances, but could yield a small error for large and small n-alkane members. Secondly, comparisons will be made later in this paper to the amount of compounds that are not n-alkanes, whose response is known to be different than the n-alkanes. Again this will produce an error of unknown magnitude, but is impossible to overcome without doing a painstaking calibration of all peaks present. This calibration would not be useful in this case, because the conclusions presented here would still be the same.

All results are summarized in graphical form in Figures 1 to 8. Each graph shows the comparison of the relative content of n-alkanes between two fractions. Each bar represents the arithmetic difference between the percentage content of that n-alkane in the two fractions being compared. A description appears directly on each graph as to which side represents greater concentrations in what fraction. The weathering of oils is shown in the C_9 to C_{13} portion of these graphs. The amount of these compounds present in either the undispersed oil remaining on the top or in the water column is on average less than that in the starting oil. Each of the compounds, up to about C_{13} is about 5% less in abundance than the starting oil. This analysis

Figure 1 Alkane Composition Comparison: Enersperse 700 in the Water

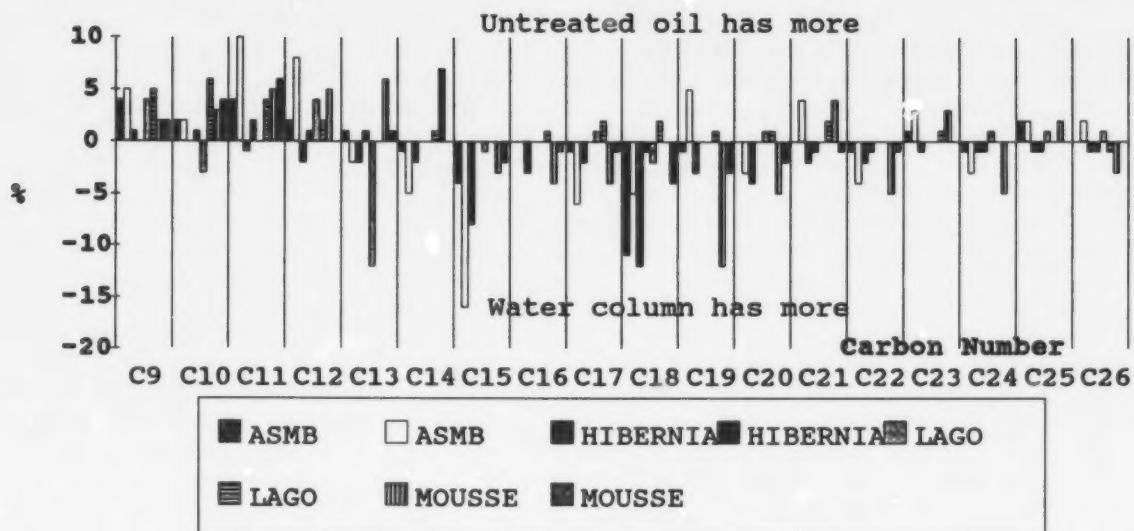


Figure 2 Alkane Composition Comparison: Experimental Dispersant in Water

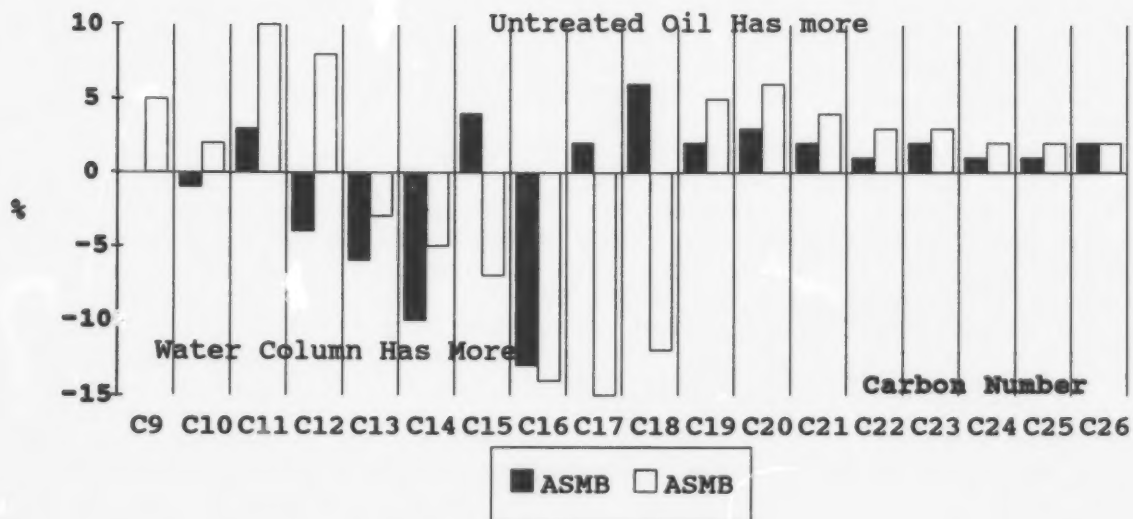


**Figure 3 Alkane Composition Comparison: Corexit 9527
in Water**

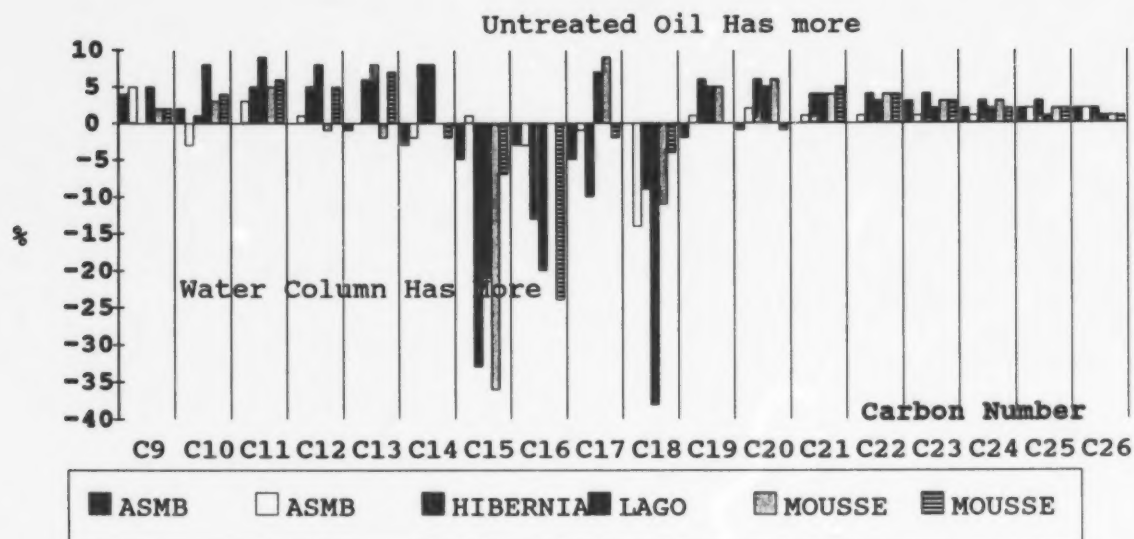


**Figure 4 Alkane Composition Comparison: Enersperse
700 and Oil on Top**

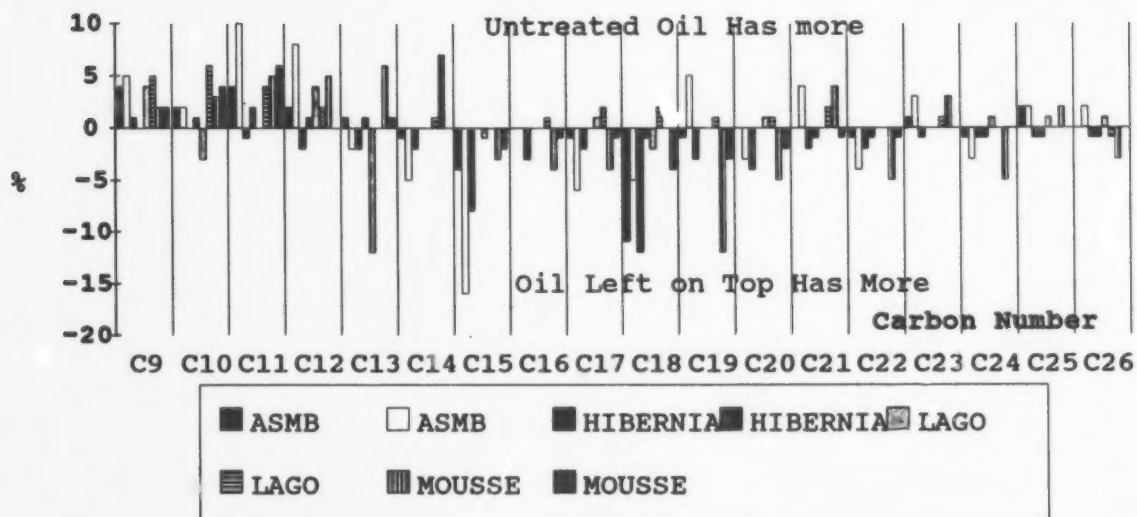


Figure 5 Alkane Composition Comparison: Corexit 9527 and Oil Left on Surface

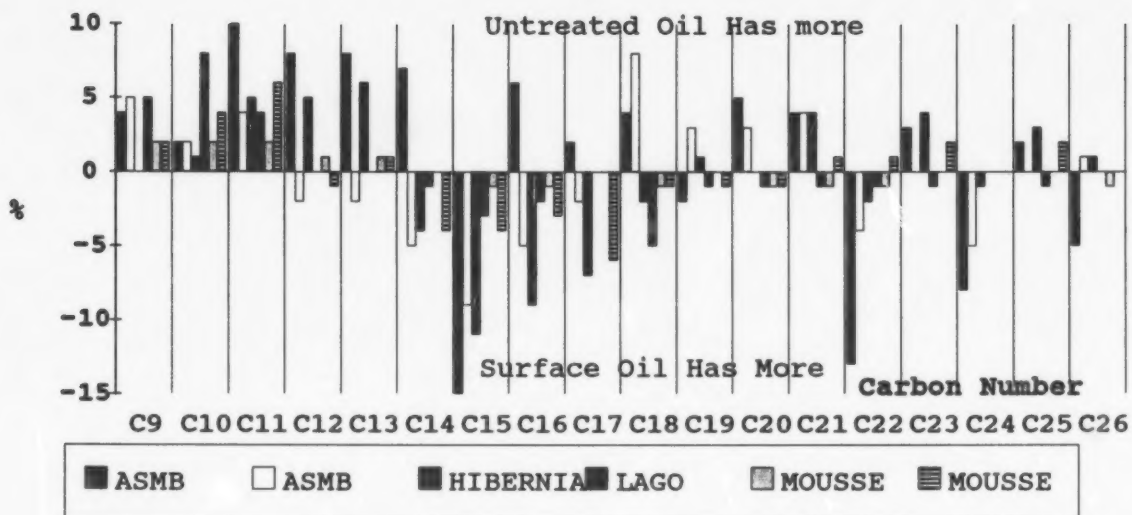


Figure 6 Alkane Composition Comparison: Experimental Dispersant and Oil Left on Surface

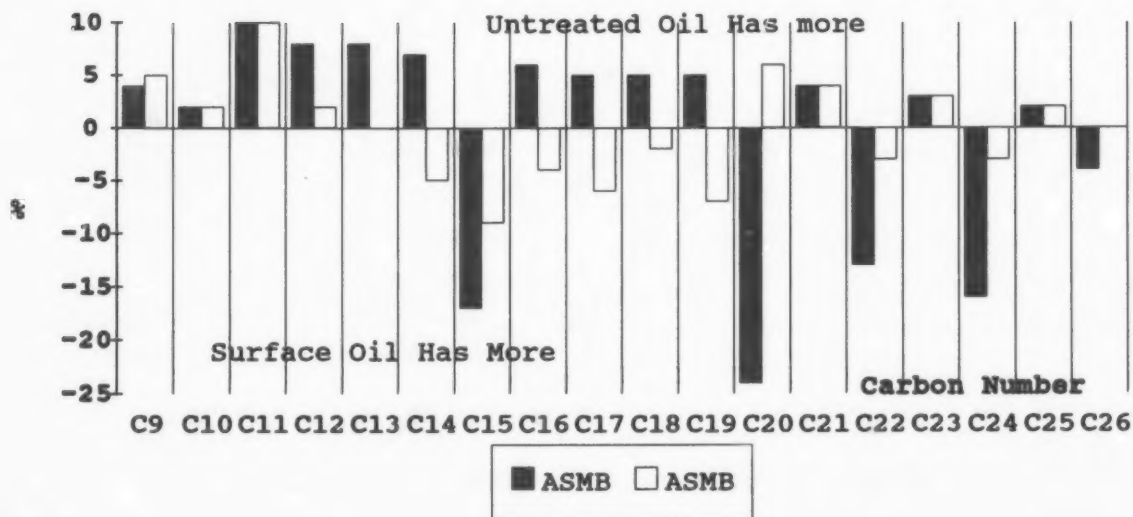


**Figure 7 Alkane Composition Comparison: Adgo Crude
in water**

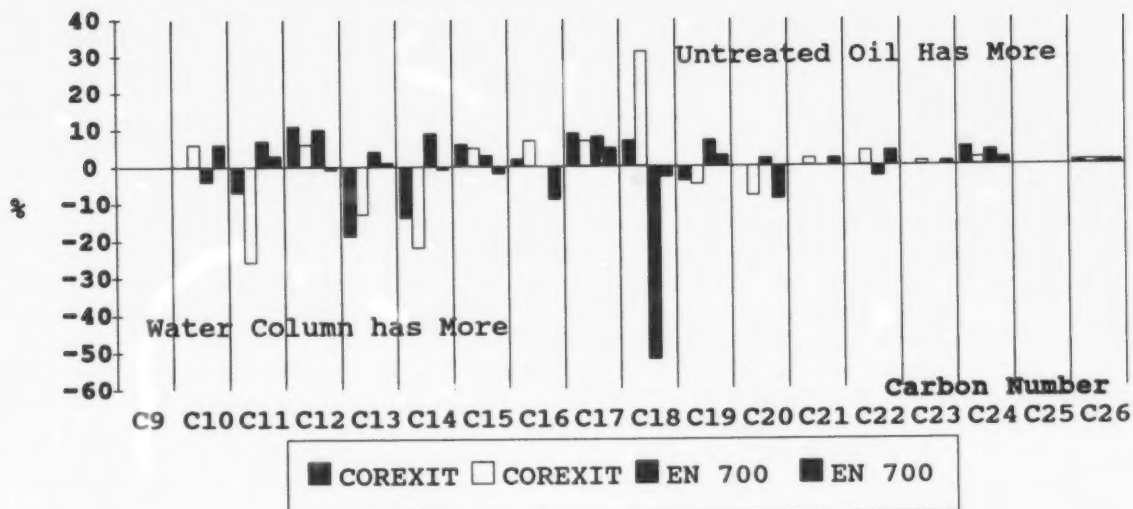
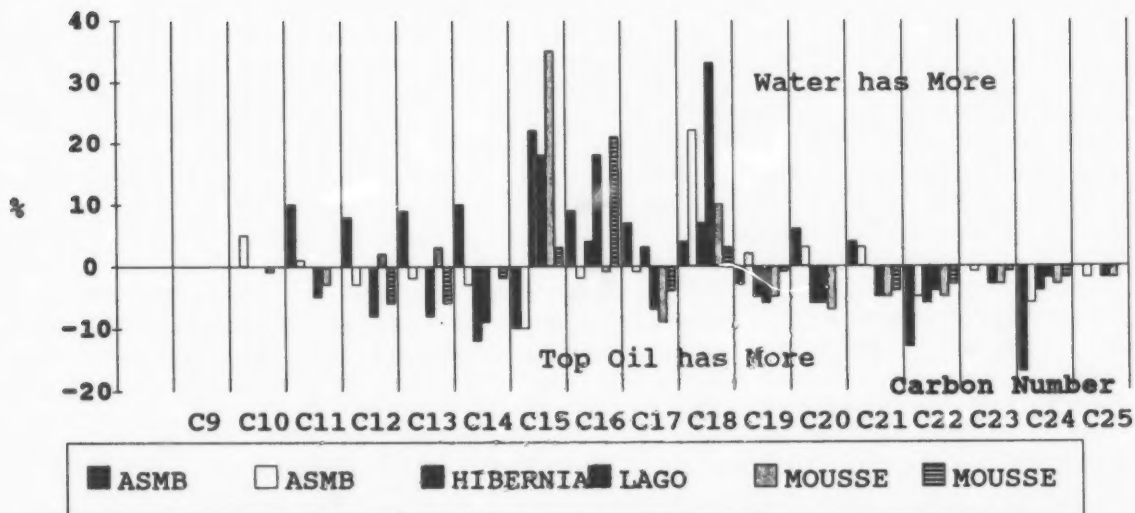


**Figure 8 Alkane Composition Comparison: Corexit 9527
in water and on top**



shows that accelerated weathering is taking place, even of the n-alkane fractions. The gas chromatographs for the same region of GC analysis show a strong decrease in other compounds present in the water or the undispersed oil remaining on the surface, compared to that of the untreated oil. This indicates that these compounds, largely aromatics, are almost totally removed from the oil during the dispersion process.

Alkane Composition Changes

Three forms of compositional differences have been found:

1. The C_9 to C_{13} n-alkanes in both the undispersed oil remaining on the surface and those in the water column are in lower concentrations than in the starting oil. This is the accelerated weathering as described above.

2. The concentration of certain n-alkanes between C_{13} and C_{18} is much greater in the water column than in the starting oil and is depleted in the surface oil.

3. The concentration of n-alkanes between C_{19} and C_{26} is slightly greater in the undispersed surface oil, than in the untreated oil and the dispersed oil.

These selectivities are illustrated in Figures 1 through 8. Each figure presents a bargraph of the concentration difference at a particular carbon number, between the untreated oil, the oil left on the surface or oil in the water column. Annotation appears on each graph to show which portion of the oil has a greater concentration. The different bars on each graph represent the different crude oils and the key to which oil it is, appears on the bottom of the graph. For most oils two runs were performed and both data sets are presented on the graphs to show the repeatability of these duplicate runs. The exception to this is the separate graph run for Adgo crude, Figure 7, where the different bars represent different dispersants. Adgo has a low n-alkane content and although it shows the same results as other oils, those results are near noise level, which is about 5%.

Figure 1 shows the comparison of n-alkane composition between the untreated oil and the oil in the water column for the dispersant Enersperse 700. This graph shows the three forms of composition change and especially the significant concentration of the C_{13} to C_{18} in the water column compared to the oil used for the experiment. Figure 2 shows a similar effect for an experimental dispersant and Figure 3 shows this effect for Corexit 9527. This latter figure shows the three forms of n-alkane concentration changes very clearly. The difference in dispersants is also illustrated here by comparing the first three figures. Corexit 9527 puts an increased amount of C_{15} , C_{16} and C_{18} into the water column. Enersperse puts an increased amount of C_{13} to C_{19} into the water column. The experimental dispersant does the same except for one carbon number lower than Enersperse. This selection is so unique that one can actually identify which dispersant was used by simple examination of the gas chromatograph.

Figures 4 to 6 show the comparison of the untreated oil with oil left on the top of the water. The alkane selectivity is

again evident. The surface oil is depleted in C_9 to C_{12} n-alkanes by accelerated weathering, is somewhat depleted in some of the C_{13} to C_{19} components which are concentrated in the water column and finally the surface oil is enriched in the larger n-alkanes which disperse poorly. Figure 7 shows the same effect with Adgo oil. Figure 8 shows a comparison of oil remaining on the surface versus oil in the water column. Since both fractions have undergone accelerated weathering by dispersant action, the lower alkanes' concentration is not significant. The dispersed oil has more C_{15} , C_{16} and C_{18} as is typical of Corexit 9527. The surface oil shows an increased concentration of larger alkanes well.

These data show that the concentrations of n-alkanes in the dispersed oil and oil left on the surface are altered by the use of surfactants. Two areas of alteration are strongly evident, one falling in carbon numbers 12 to 18 and the other above these values. The former is directly indicative of the type of dispersant used, and in fact could be used to identify the specific dispersant. This selectivity is thought to be a result of absorption of n-alkanes to the oleophilic portion of the surfactant. This occurs at the same chain length as the oleophilic portion or 1 or 2 carbon units shorter. Such phenomena has been observed before and actually is used in designing surfactants for solubilizing materials.¹⁹ It has however never been reported or studied in terms of oil spill dispersants.

The concentrations of the higher alkanes (C_{19} and above) are lower in the dispersed oil than in the starting oil and in the surface oil. This indicates that these components are less dispersable than the shorter alkanes and are concentrated in the undispersed surface layer.

The overall effect of this selectivity is thought to be significant upon the final dispersion effectiveness, but not dominating. Table 3 shows the approximate concentrations of the n-alkanes in the three studied fractions. There appears to be an n-alkane enrichment overall in the water column caused by

Table 3 Alkane Content

(Content Determined by GC Analysis of Weathered Fraction only)

Oil	Dispersant	n-Alkane Content (%)			Alkane Enrichment (%)	
		Oil	Water	Top	Water	Top
Adgo	Corexit	13	13	25	0	-
	Enersperse	13	37	55	184	-
ASMB	Experimental	43	54	44	26	2
	Corexit	43	68	33	58	-23
	Enersperse	43	66	45	53	5
Hibernia	Corexit	48	44	44	-8	-8
	Enersperse	48	60	47	25	-2
Lago Medio	Corexit	40	87	53	118	32
	Enersperse	40	56	38	40	-5
Mousse Mix	Corexit	44	81	44	84	0
	Enersperse	44	74	54	68	23
				Average	59	1

dispersants. The average alkane enrichment is 59%. The n-alkane fraction content in the surface oil remains about the same. This is consistent with the previous finding, as the depletion of the C_{13} to C_{19} fraction by dispersant action is matched by the increased amount of the larger n-alkanes left on the surface.

The effectiveness of the three dispersants used in this test are in decreasing order; experimental, Enersperse 700 and Corexit 9527. The amount of n-alkanes selected by each of these dispersants decreases in the same order. The experimental dispersant which has a large mixture of chain lengths and therefore concentrates the greater number of different n-alkanes in the water column, is the most effective. There may be a correlation between these facts and that may be a hint for the dispersant designer seeking to improve dispersant effectiveness.

Summary and Conclusions

Dispersants cause accelerated weathering of oil, removing most of the oil components up to C_{12} . The acceleration consists of the removal of about 11% of the oil mass on the short term. Most of the aromatics and some of the n-alkanes are removed.

Dispersants absorb some of the n-alkanes corresponding to their surfactant oleophilic chain lengths, this results in an increased concentration of these compounds in the water column and their depletion in the slick remaining on the surface. This selectivity is unique to the dispersant formulation.

Dispersants do not have as much effect on longer chain n-alkanes ($>C_{19}$) as they do on the shorter ones. The surface oil is enriched in these longer chain n-alkanes.

These three effects, although significant, are not major and do not dominate the dispersion process.

These findings do however, have implications for dispersant design. There appears to be a correlation between the number of different chain lengths in a surfactant (and consequently the n-alkanes concentrated in the water column oil) and the effectiveness. The more surfactant chain lengths present, the greater the effectiveness. Furthermore the finding that the surface oil contains higher concentrations of longer-chain alkanes indicates that this oil is less dispersable than before and also that future dispersant formulation work might concentrate on dispersing more of these compounds into the water.

The fact that dispersants promote accelerated weathering also has implications. First, the application of remote sensing to measure oil dispersion on the sea should include consideration of the additional amount removed by accelerated weathering. Secondly, the removal of the volatile fractions of the oil, many of which are toxic aromatic compounds, implies that over short time periods chemically-dispersed oil would be somewhat less toxic to many organisms than mechanically-dispersed oil at the same concentration.

Acknowledgements

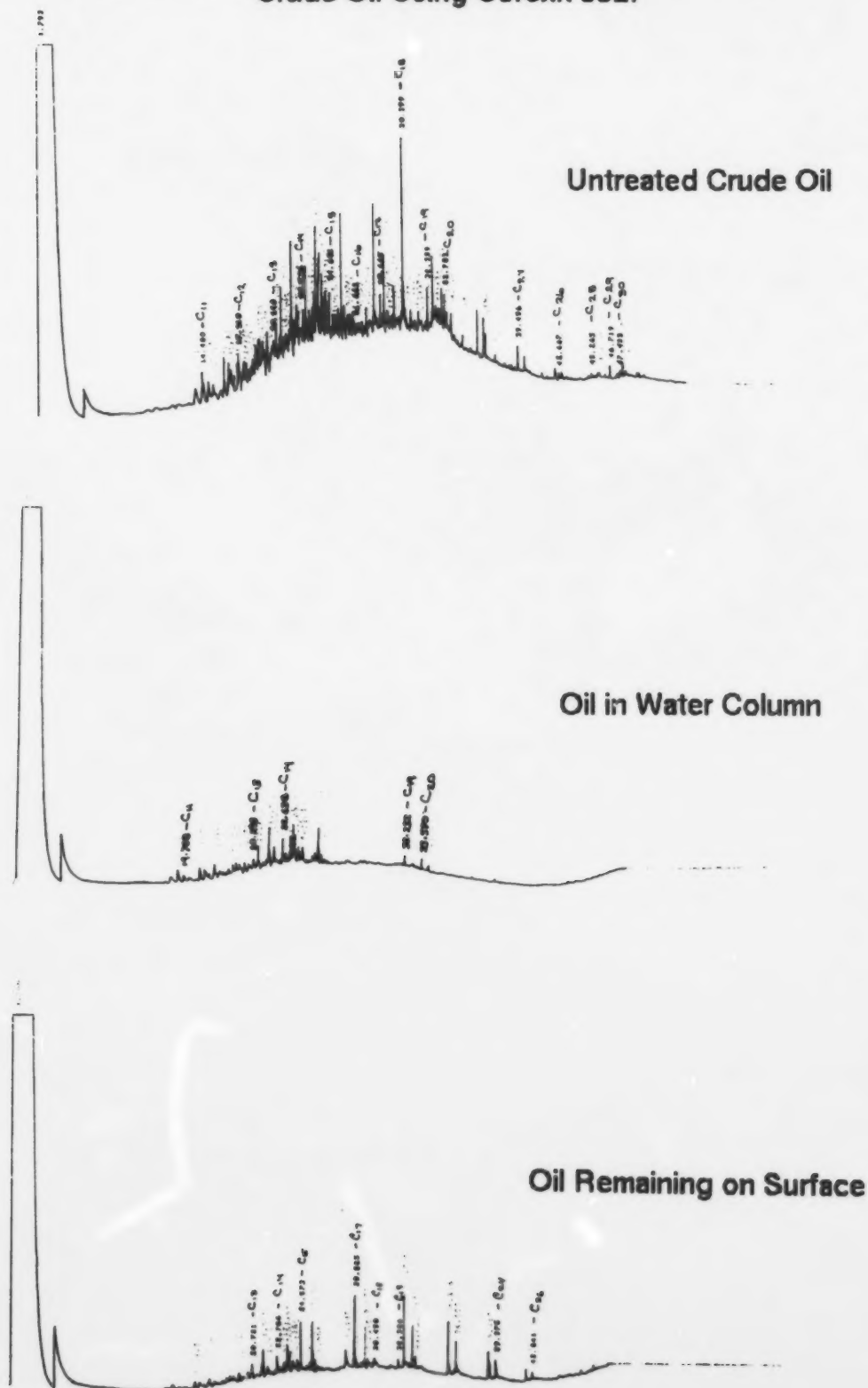
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Figure A1 Chromatograms of the Dispersion of Adgo Crude Oil Using Corexit 9527



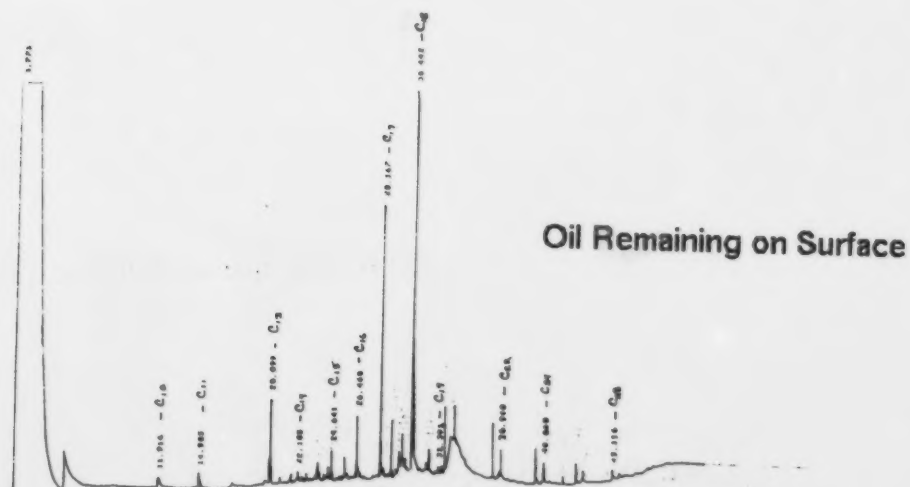


Figure A3 Chromatograms of the Dispersion of ASMB Crude Oil Using Experimental BQ

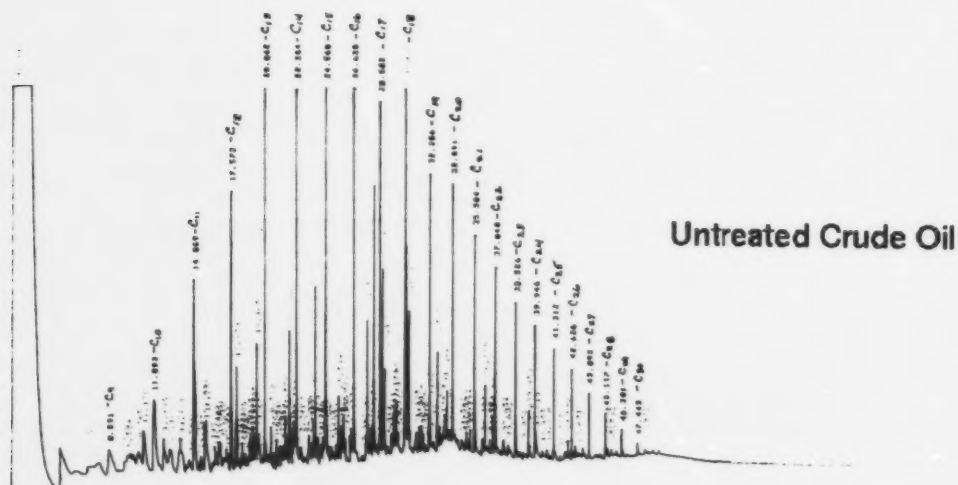


Figure A4 Chromatograms of the Dispersion of ASMB Crude Oil Using Corexit 9527

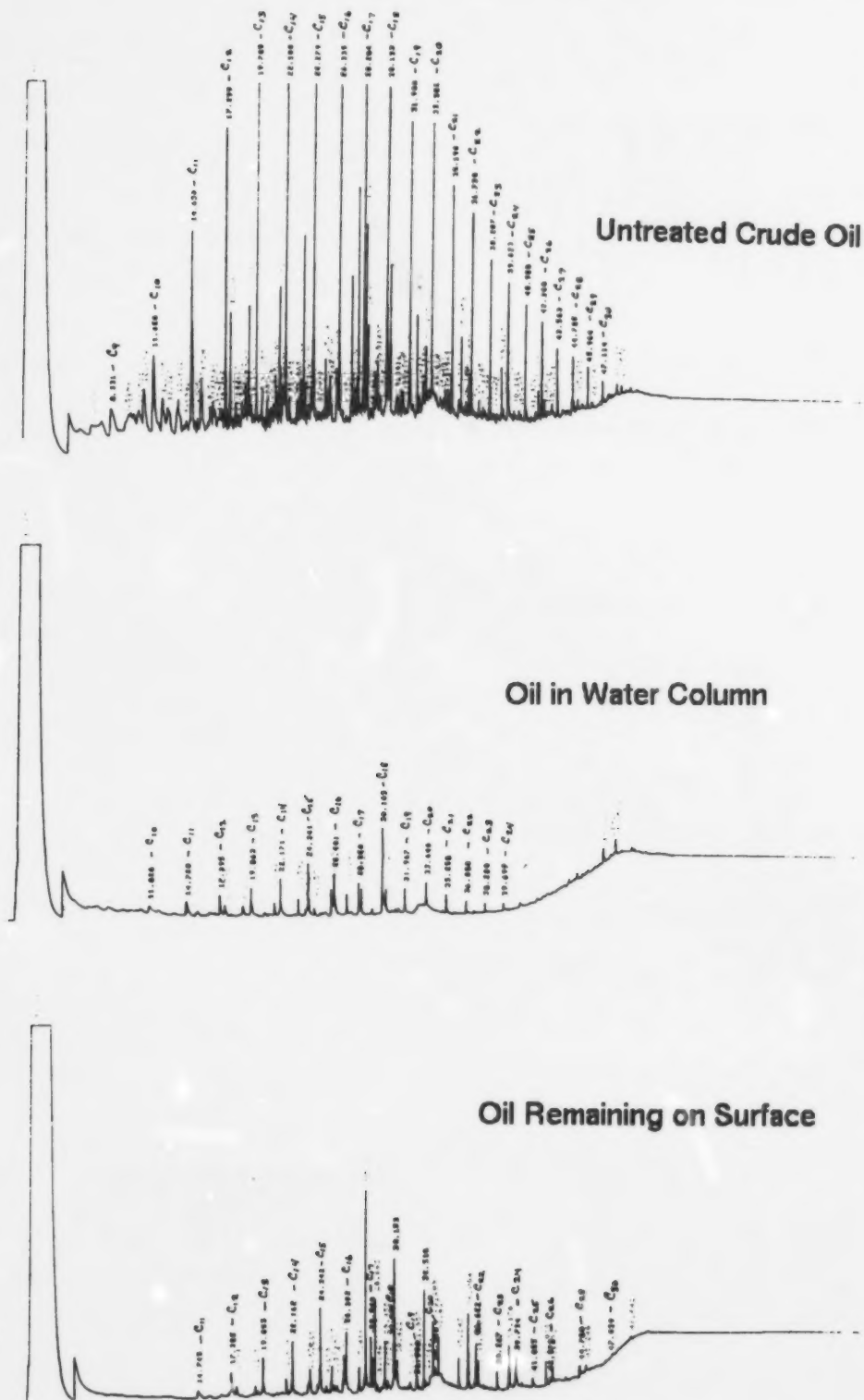


Figure A5 Chromatograms of the Dispersion of ASMB
Crude Oil Using Enersperse 700

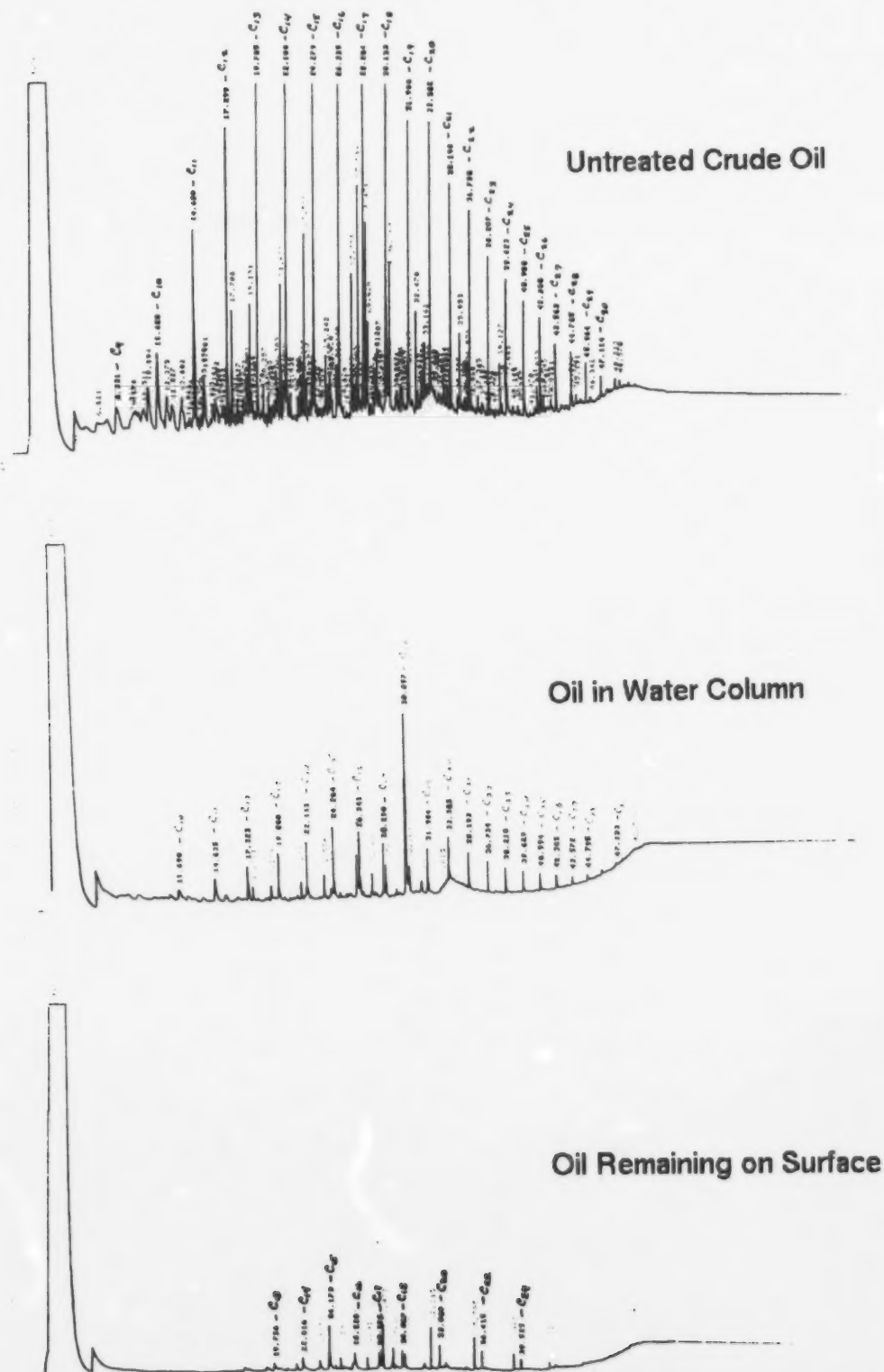


Figure A6 Chromatograms of the Dispersion of Hibernia Crude Oil Using Corexit 9527

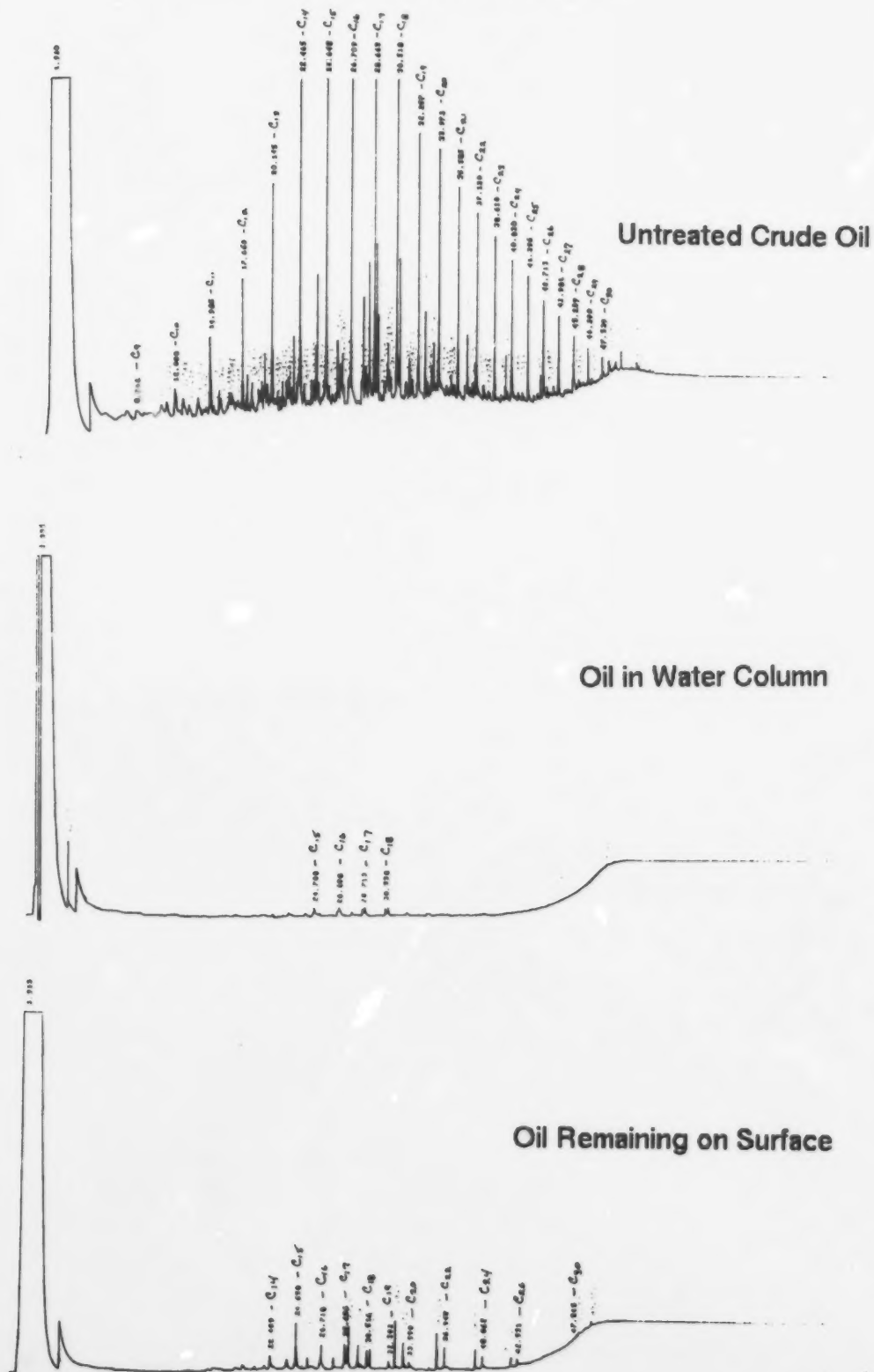


Figure A7 Chromatograms of the Dispersion of Hibernia Crude Oil Using Enersperse 700

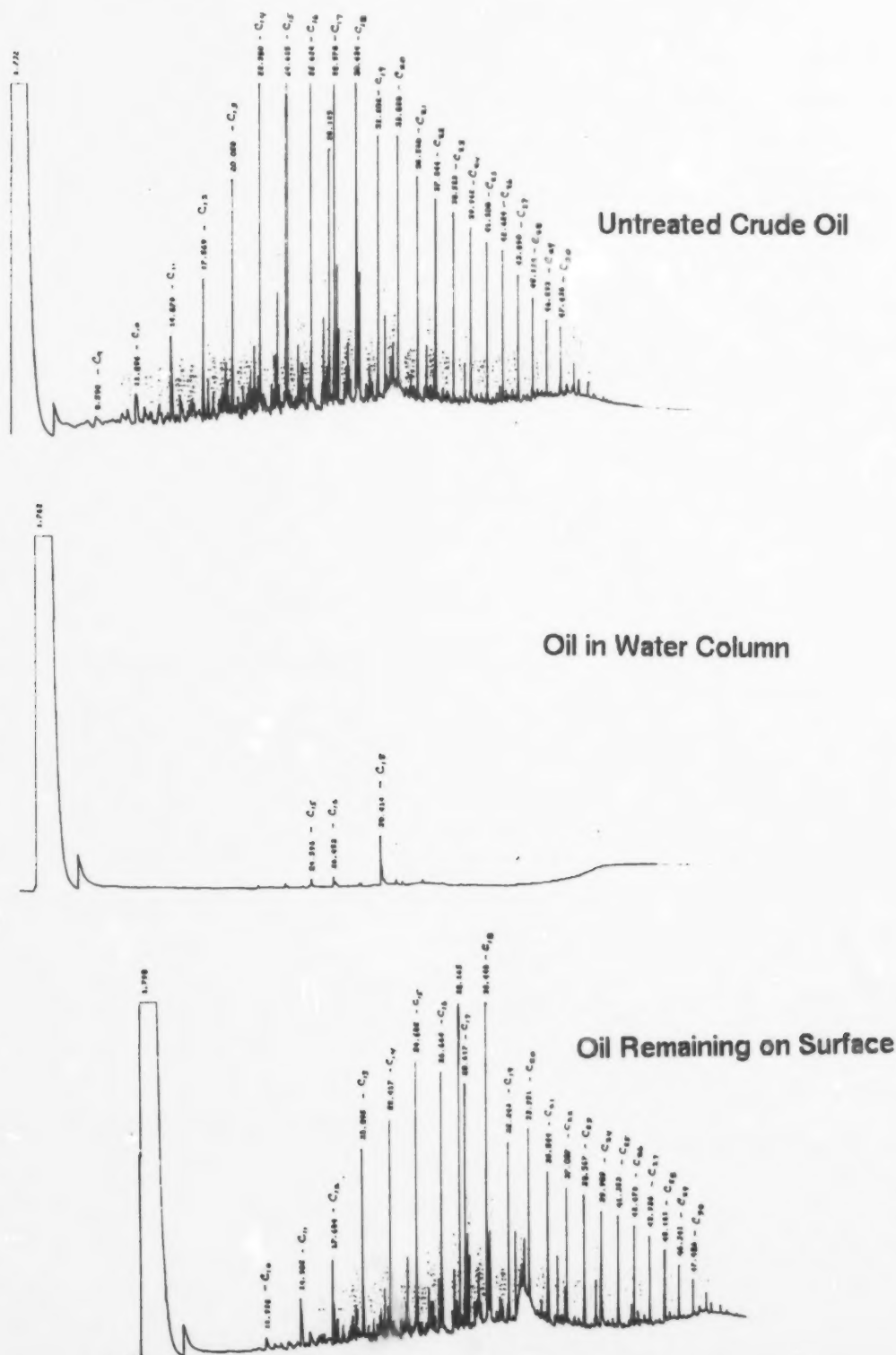


Figure A8 Chromatograms of the Dispersion of Lago Medio Crude Oil Using Corexit 9527

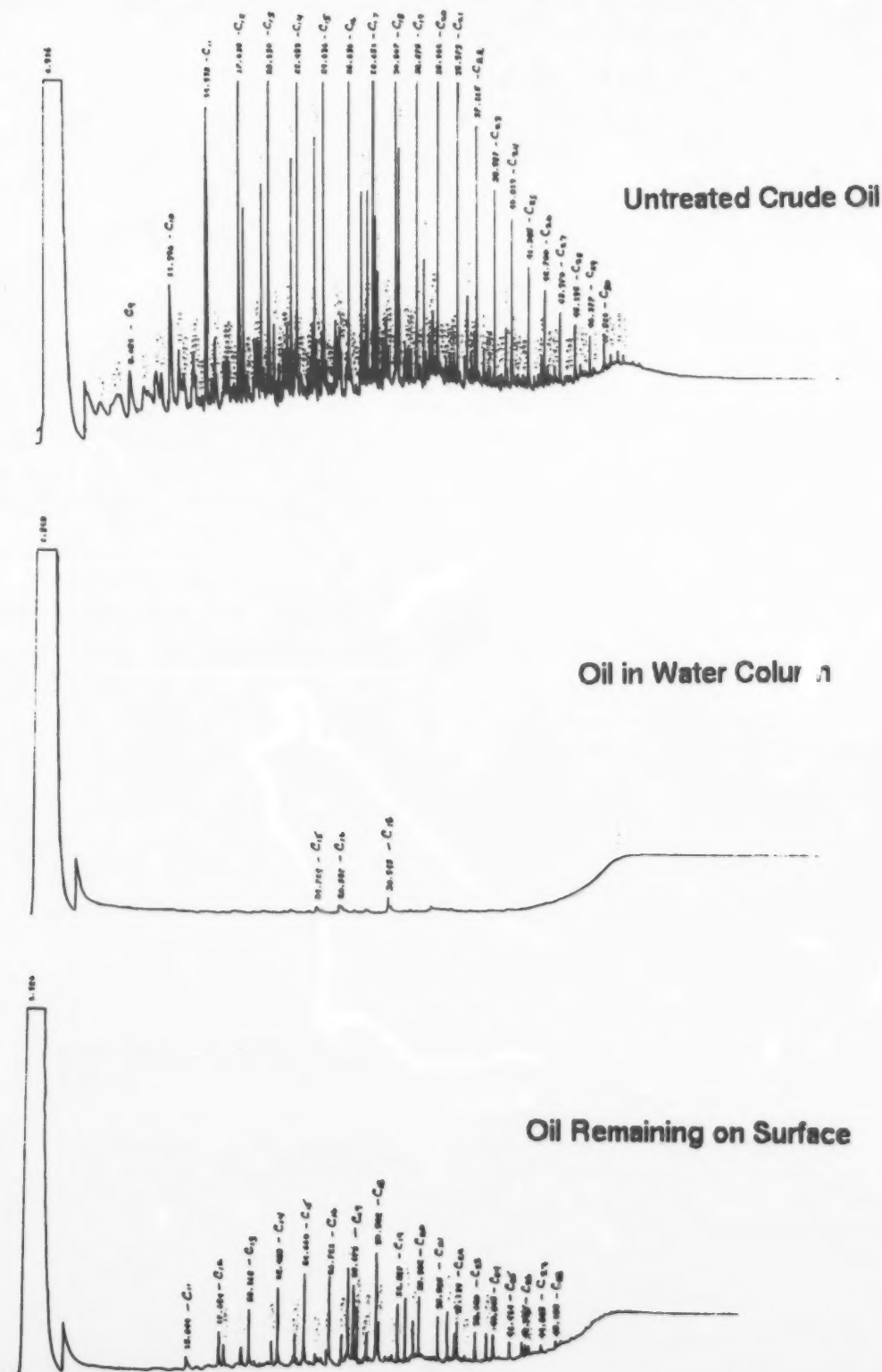
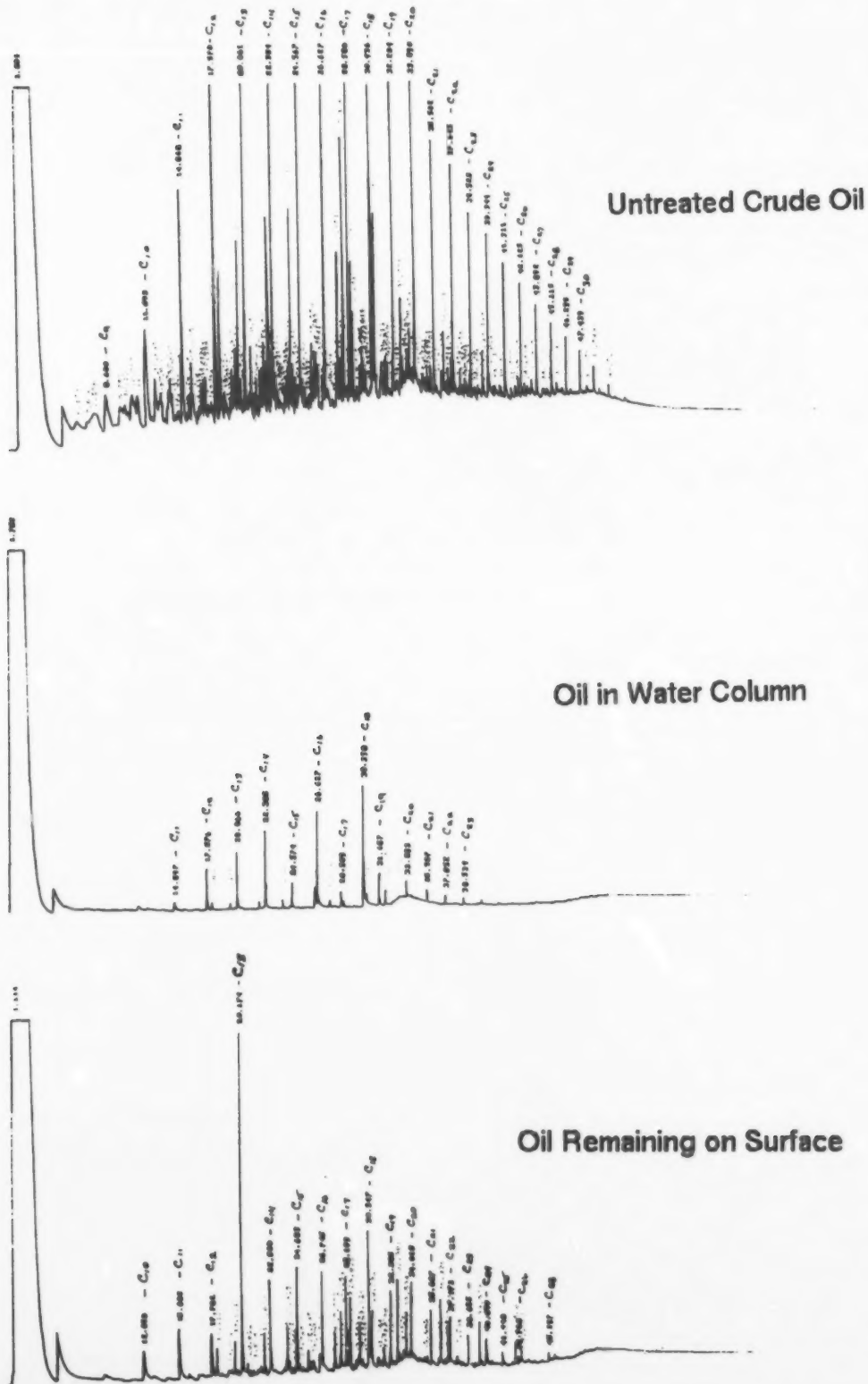


Figure A9 Chromatograms of the Dispersion of Lago Medio Crude Oil Using Enersperse 700



Chromatograms of the Dispersion of Mousse Mix Crude Oil Using Corexit 9527

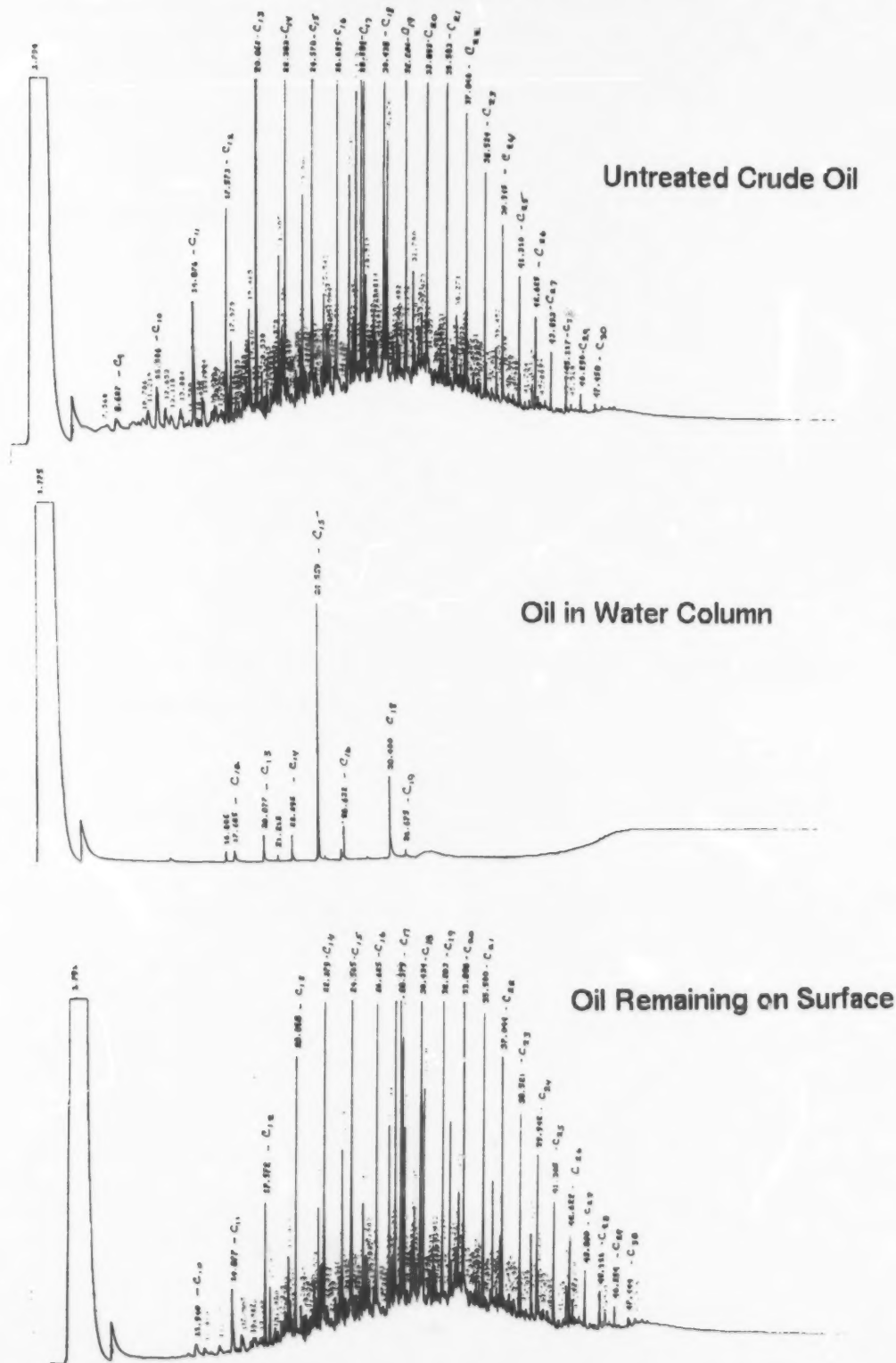


Figure A11 Chromatograms of the Dispersion Of Mousse Mix Crude Oil Using Enersperse 700

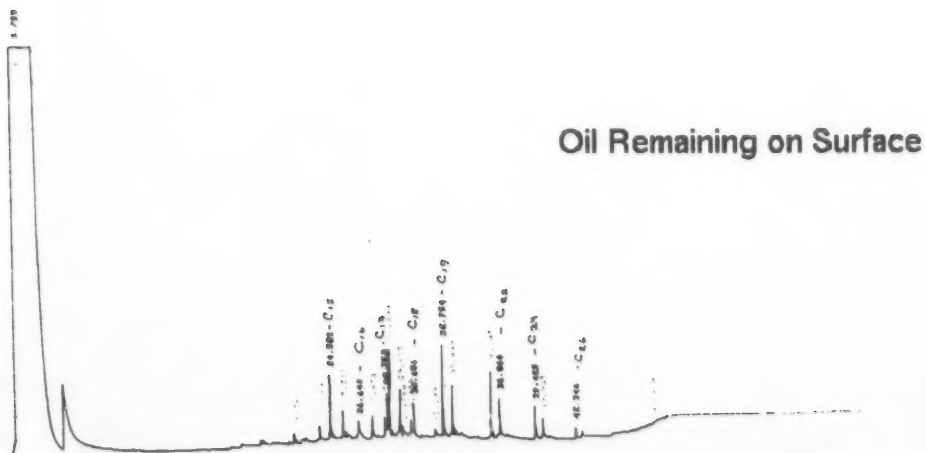
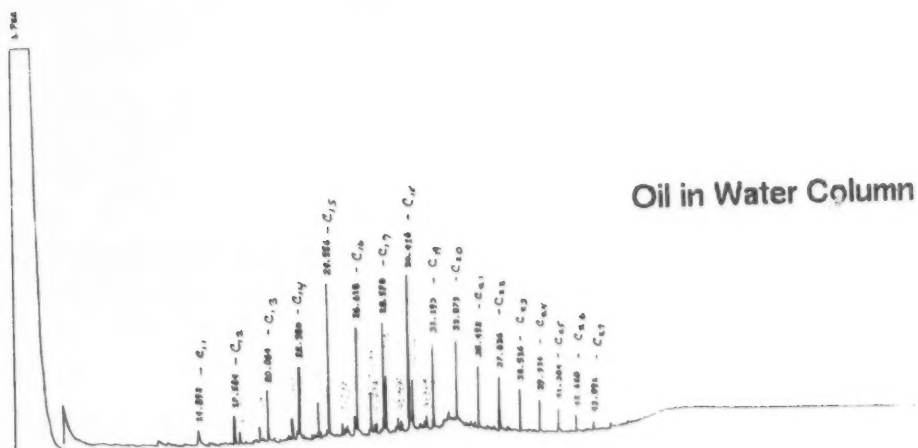
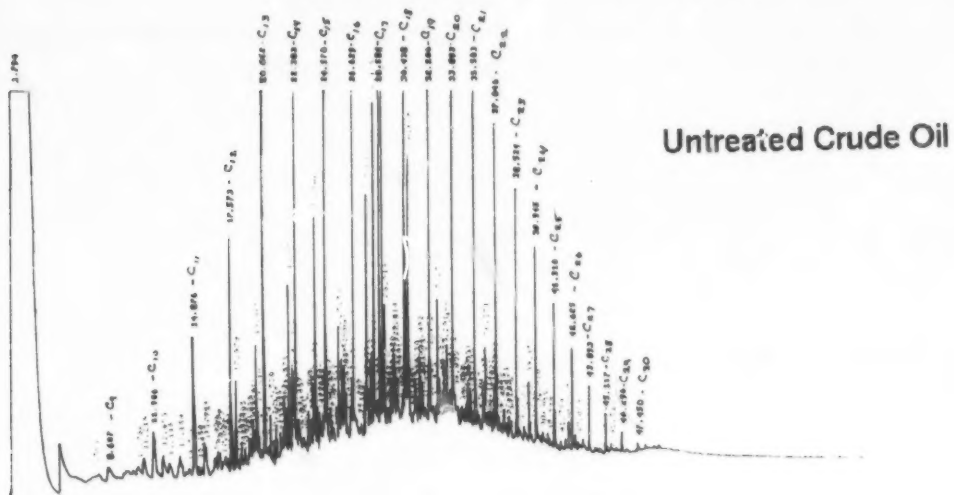


Table A1 CHANGES IN WATER ALKANE COMPOSITION AFTER DISPERSION

COREXIT 9527		PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	
ASMB	4	2	0	0	-1	-3	-5	-3	-5	0	-2	-1	0	0	3	2	2	2	
ASMB	5	-3	3	1	0	-2	1	-3	-1	-14	1	2	1	1	1	1	2	2	
HIBERNIA	0	1	5	5	6	8	-33	-13	-10	-9	6	6	4	4	4	3	3	2	
LAGO	5	8	9	8	8	8	-21	-20	7	-38	5	5	4	3	2	2	1	1	
MOUSSE	2	3	5	-1	-2	0	-36	0	9	-11	5	6	4	4	3	3	2	1	
MOUSSE	2	4	6	5	7	-2	-7	-24	-2	-4	0	-1	5	4	3	2	2	1	

EN 700		PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	
ASMB	4	-2	6	-7	5	4	-8	1	-5	-10	-3	0	2	0	2	2	2	2	
ASMB	5	-3	3	3	3	0	2	0	1	-16	1	0	1	0	1	0	0	1	
HIBERNIA	1	2	3	2	3	4	3	-13	4	-63	3	3	2	2	2	2	2	2	
HIBERNIA	0	1	5	5	6	8	11	-29	8	-55	6	6	4	4	4	3	3	2	
LAGO	4	7	5	-3	-4	-6	4	-10	3	-16	-1	3	1	1	0	2	2	2	
LAGO	5	8	9	8	8	8	-91	6	7	7	5	5	4	3	2	2	1	1	
MOUSSE	2	3	1	1	1	0	1	0	-1	-5	0	-1	-1	0	0	0	0	0	
MOUSSE	2	4	6	5	2	-1	-1	-2	-3	-11	-2	-2	-1	-1	0	2	2	1	

EXPT'L BQ		PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	
ASMB	0	-1	3	-4	-6	-10	4	-13	2	6	2	3	2	1	2	1	1	2	
ASMB	5	2	10	8	-3	-5	-7	-14	-15	-12	5	6	4	3	3	2	2	2	

Table A2 CHANGES IN SURFACE ALKANE COMPOSITION AFTER DISPERSION

COREXIT 9527 PERCENTAGE CHANGE BY CARBON NUMBER

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	10	8	8	7	-15	6	2	4	-2	5	4	-13	3	-8	2	-5
ASMB	5	2	4	-2	-2	-5	-9	-5	-2	8	3	3	4	-4	0	-5	0	1
HIBERNIA	0	1	5	5	6	-4	-11	-9	-7	-2	1	0	4	-2	4	-1	3	1
LAGO	5	8	4	0	0	-1	-3	-2	0	-5	-1	-1	-1	-1	-1	0	-1	0
MOUSSE	2	2	2	1	1	0	-1	-1	0	-1	0	-1	-1	-1	0	0	0	-1
MOUSSE	2	4	6	-1	1	-4	-4	-3	-6	-1	-1	-1	1	1	2	0	2	0

EN 700 PERCENTAGE CHANGE BY CARBON NUMBER

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	4	2	1	-1	-4	0	-1	-11	-1	0	0	-1	1	-1	2	0
ASMB	5	2	10	8	-2	-5	-16	0	-6	-5	5	-3	4	-4	3	-3	2	2
HIBERNIA	1	0	-1	-2	-2	-2	-8	-3	-2	-12	-3	-4	-2	-2	-1	-1	-1	-1
HIBERNIA	0	1	2	1	1	0	0	0	0	-1	0	0	-1	-1	0	-1	-1	-1
LAGO	4	-3	0	4	-12	0	-1	0	1	-2	0	1	0	0	0	1	1	1
LAGO	5	6	4	2	0	1	0	1	2	2	1	1	2	0	1	0	0	-1
MOUSSE	2	3	5	5	6	7	-3	-4	-4	0	-12	-5	4	-5	3	-5	2	-3
MOUSSE	2	4	6	0	1	0	-2	-1	-1	-4	-3	-2	-1	-1	0	0	0	0

EXPT'L BQ PERCENTAGE CHANGE BY CARBON NUMBER

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	10	8	8	7	-17	6	5	5	5	-24	4	-13	3	-16	2	-4
ASMB	5	2	10	2	0	-5	-9	-4	-6	-2	-7	6	4	-3	3	-3	2	0

Table A3 **CHANGES IN ALKANE COMPOSITION AFTER DISPERSION**
ADGO

PERCENTAGE CHANGE BY CARBON NUMBER (WATER)

DISPERSANT	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
COREXIT 95270	0	-7	11	-19	-14	6	2	9	7	-4	0	0	0	0	5	0	1	
COREXIT 95270	6	-26	6	-13	-22	5	7	7	31	-5	-8	2	4	1	2	0	1	
EN 700	0	-4	7	10	4	9	3	0	8	-52	7	2	0	-3	0	4	0	1
EN 700	0	6	3	-1	1	-1	-2	-9	5	-3	3	-9	2	4	1	2	0	1

PERCENTAGE CHANGE IN CARBON NUMBER (SURFACE)

DISPERSANT	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
COREXIT 95270	6	8	6	4	-1	-6	7	-20	31	-24	5	2	4	1	-11	0	-5	
COREXIT 95270	0	12	11	-6	2	-16	2	-19	-1	6	12	0	0	0	-4	0	-3	
EN 700	0	-4	9	11	2	10	2	-5	-13	-34	9	12	0	-3	0	3	-1	-1
EN 700	0	6	8	6	4	1	-3	-8	-11	1	3	-4	2	-1	1	-3	0	-2

Table A4 DIFFERENCE IN ALKANE COMPOSITION BETWEEN THE WATER
AND THE SURFACE OIL (+VE WATER HAS MORE)

EXPT'L BQ	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	0	0	-6	3	0	-2	10	9	10	-12	0	0	-6	0	-5	0	-2
ASMB	4	3	7	12	14	17	-21	19	3	-1	3	-27	2	-14	1	-17	1	-6

EN 700	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	4	-2	9	-4	-5	4	-1	4	-1	2	0	-2	-1	-1	-3	0	-2
ASMB	0	5	7	5	-5	-5	-18	0	-7	11	4	-3	3	-4	2	-3	2	1
HIBERNIA	0	-2	-4	-4	-5	-6	7	10	-6	51	-6	-7	-4	-4	-3	-3	-3	-3
HIBERNIA	0	0	-3	-4	-5	-8	-11	29	-8	54	-6	-6	-5	-5	-4	-4	-4	-3
LAGO	0	-10	-5	7	-8	6	-5	10	-2	14	1	-2	-1	-1	0	-1	-1	-1
LAGO	0	-2	-5	-6	-8	-7	91	-5	-5	-5	-4	-4	-2	-3	-1	-2	-1	-2
MOUSSE	0	0	4	4	5	7	-4	-4	-3	5	-12	-4	5	-5	3	-5	2	-3
MOUSSE	0	0	0	-5	-1	1	-1	1	2	7	-1	0	0	0	0	-2	-2	-1

COREXIT 9527	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	0	10	8	9	10	-10	9	7	4	-3	6	4	-13	0	-17	0	-7
ASMB	0	5	1	-3	-2	-3	-10	-2	-1	22	2	3	3	-5	-1	-6	-2	-1
HIBERNIA	0	0	0	0	0	-12	22	4	3	7	-5	-6	0	-6	0	-4	0	-1
LAGO	0	0	-5	-8	-8	-9	18	18	-7	33	-6	-6	-5	-4	-3	-2	-2	-1
MOUSSE	0	-1	-3	2	3	0	35	-1	-9	10	-5	-7	-5	-5	-3	-3	-2	-2
MOUSSE	0	0	0	-6	-6	-2	3	21	-4	3	-1	0	-4	-3	-1	-2	0	-1

ADGO	PERCENTAGE CHANGE BY CARBON NUMBER																	
DISPERSANT	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
EN 700	0	0	5	7	3	2	-1	1	-16	4	0	5	0	-5	0	-5	0	-3
EN 700	0	0	2	1	-2	1	-1	-5	-21	18	2	10	0	0	0	-1	-1	-2
COREXIT 9527	0	0	19	0	13	16	-22	0	-28	-8	10	12	0	0	0	-9	0	-4
COREXIT 9527	0	0	34	0	17	21	-11	0	-27	0	-19	13	0	0	0	-13	0	-6

WATER SOLUBILITY BEHAVIOUR OF PETROLEUM MIXTURES

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INTRODUCTION

Dissolution is one of the fundamental mass transfer processes that occurs when oil is spilled on water. Although the fraction of oil that dissolves into water is relatively small when compared to the total mass of oil, it is this fraction that has intimate contact with aquatic organisms and thus is an important determinant of oil toxicity.

Oil is a complex mixture of compounds and each compound will partition differently between the aqueous and oil phases. Components with relatively high aqueous solubilities will tend to transfer to the aqueous phase while the insoluble components will stay in the oil. The term "water soluble fraction" (WSF) is commonly used to describe the aqueous solution which is formed when oil and water are brought into contact. By definition, a WSF is a single phase solution comprised of individually dissolved hydrocarbon molecules, and a WSF is free of any oil-in-water emulsions. The composition and concentration of the WSF depends upon several factors such as the composition of the oil, the properties of the water, temperature and the method of preparation. Different aspects of petroleum dissolution have been extensively studied by various researchers. (Burris (1985); Burris and MacIntyre (1985, 1986); Lockhart et al. (1984); Leinonen (1972, 1973); Mackay and Shiu (1975, 1976); Mackay et al. (1985); Maijanen et al. (1984); McAuliffe (1966, 1977); Payne et al. (1987), Price (1976); Shiu et al. (1988); Smith and Harper (1981)).

One of the most significant recent findings is that the composition and concentration of WSF's can be extremely sensitive to the water-to-oil volume ratio used during WSF preparation. (Smith and Harper (1981); Lockhart et al. (1984); Maijanen et al. (1984)). The focus of this study was to examine how the WSF composition and concentration of various petroleum mixtures depend upon the water-to-oil ratio.

EXPERIMENTAL

Materials

The following six oils were used in this study:

Prudhoe Bay Crude Oil	} API/EPA standard reference oils
South Louisiana Crude Oil	
Fuel Oil No.2 (high aromatic)	
Fuel Oil No.6, Bunker C (high viscosity)	
Western Sweet Blend Crude Oil - EPS standard oil for dispersant testing	
Regular Unleaded Gasoline - purchased in Halifax, Nova Scotia	

The water used was distilled in glass, filtered and degassed prior to use. The vessels used to prepare the WSF's were 60 mL amber glass Hypo-vials which were crimped sealed with teflon/silicone septa. All chemicals used as standards and for calibration were from Aldrich Chemical Company and were 99+% pure.

Preparation of Water Soluble Fractions

WSF's were prepared at 25°C using water-to-oil volume ratios from 5:1 to 10,000:1. Oil was slowly injected through a 10 cm long needle into an inverted, sealed Hypo-vial which was completely filled with water; water displaced by the oil flowed out through a second needle. The vials were placed on a gyrotory shaker table within a psychrotherm and mixed at 30 RPM. This mixing speed was not of sufficient energy to cause a major deformation of the oil/water interphase. The oil/water system was allowed to equilibrate for at least 20 days.

This method of WSF preparation resulted in solutions of excellent reproducibility (standard deviations of $< 3\%$) and avoided two common difficulties encountered during WSF preparation: (i) loss of compounds by volatilization and (ii) formation of oil-in-water emulsions.

Water Soluble Fraction Analysis

Aqueous samples were analyzed by a purge-and-trap/GC technique, using a Tekmar Model 4000 Dynamic Headspace Concentrator coupled to a cyrofocusing Tekmar Model 1000 Capillary Interphase and a temperature programmed Hewlett-Packard Model 5890 Gas Chromatograph equipped with a flame-ionization-detector and a SPB-1 fused silica capillary column (0.53 mm ID X 30 m long). Calibration and compound identification were performed with saturated solutions of pure hydrocarbons.

RESULTS AND DISCUSSION

Figures 1 to 6 show the change in WSF concentration as a function of water-to-oil ratio for the six test oils. Each figure shows the total WSF concentration and the concentrations of major WSF components. Figures 1, 2 and 3 show the concentration curves for WSF's produced by the three crude oils, Western Sweet Blend, South Louisiana and Prudhoe Bay. The dependence of the WSF on the water-to-oil ratio are very similar for the crude oils with minor differences in the relative abundance of some compounds. At low water-to-oil ratios, the WSF's are mainly comprised of benzene, toluene, ethylbenzene and xylenes (at a water-to-oil ratio of 5, these components account for about 80% of the total WSF). As the water-to-oil ratio increases, the concentration of these compounds decreases and their relative proportions change. At a water-to-oil ratio of 10,000, these compounds account for about 15 to 30% of the total WSF. Benzene is the predominant compound in the WSF at low water-to-oil ratios (less than 100). As the water-to-oil ratio approaches 100, toluene becomes the predominant species. As the ratio is increased further (say up to 10,000) no species of compounds predominates, but instead the WSF is made of many individual compounds, each accounting for only a small fraction of the WSF's composition. The concentration of the less soluble compounds, such as C3 benzenes and naphthalene, are far less dependent upon the water-to-oil ratio than the more soluble compounds. Their concentration remains relatively constant over the range of water-to-oil ratios tested while the concentration of the more soluble compounds showed a dramatic decrease as the ratio increased. Therefore, the less soluble compounds in the oil account for a larger proportion of the compounds present in WSF's prepared at larger water-to-oil ratios.

Figure 4 shows the composition and concentration of WSF's prepared from gasoline. The general form of the curves are similar to those of the crude oils except the concentrations of the volatile aromatics are significantly higher and the less volatile materials (above naphthalene) are absent.

Figure 1: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Western Sweet Mixed Blend Crude Oil

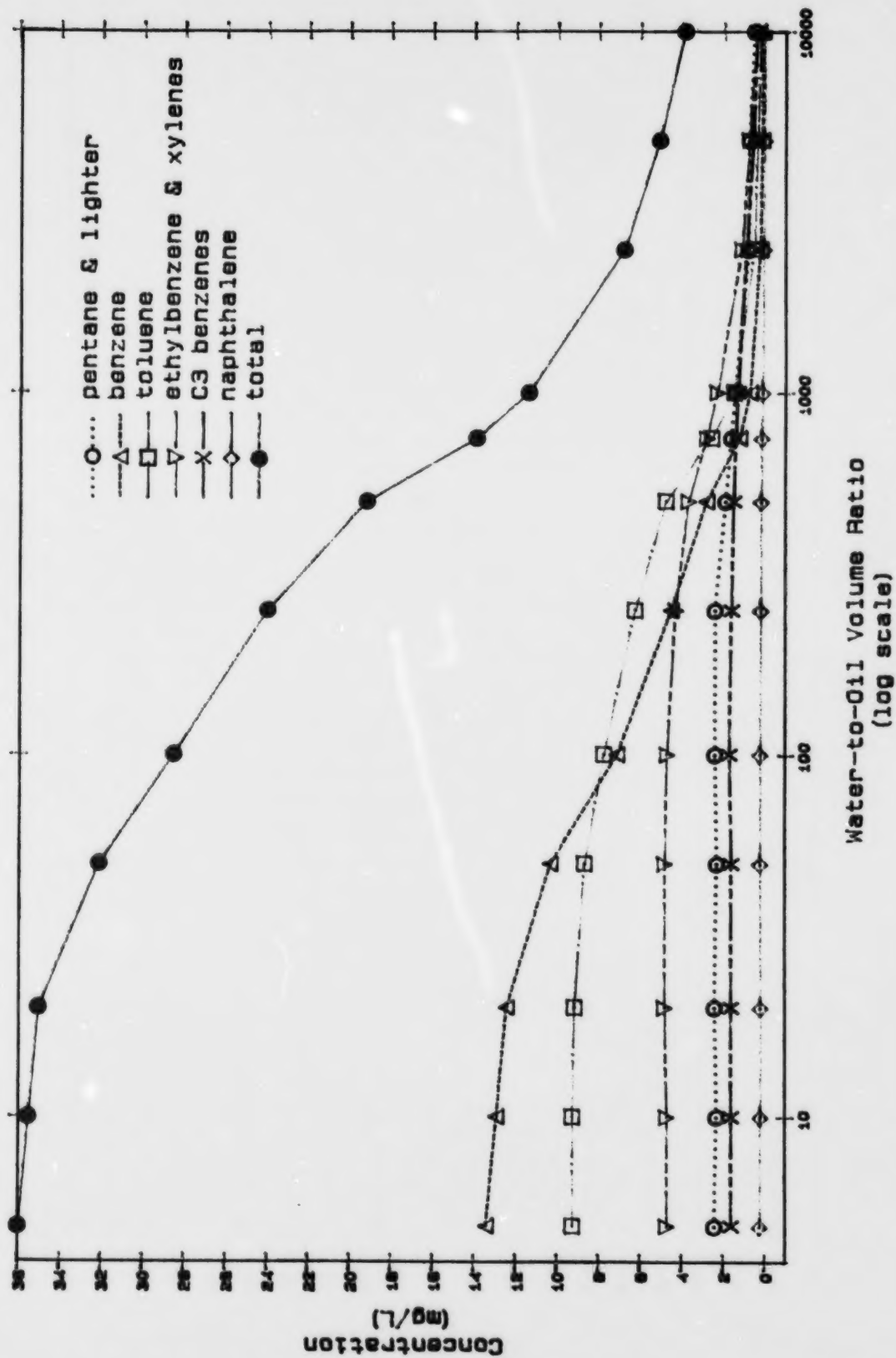


Figure 2: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
South Louisiana Crude Oil

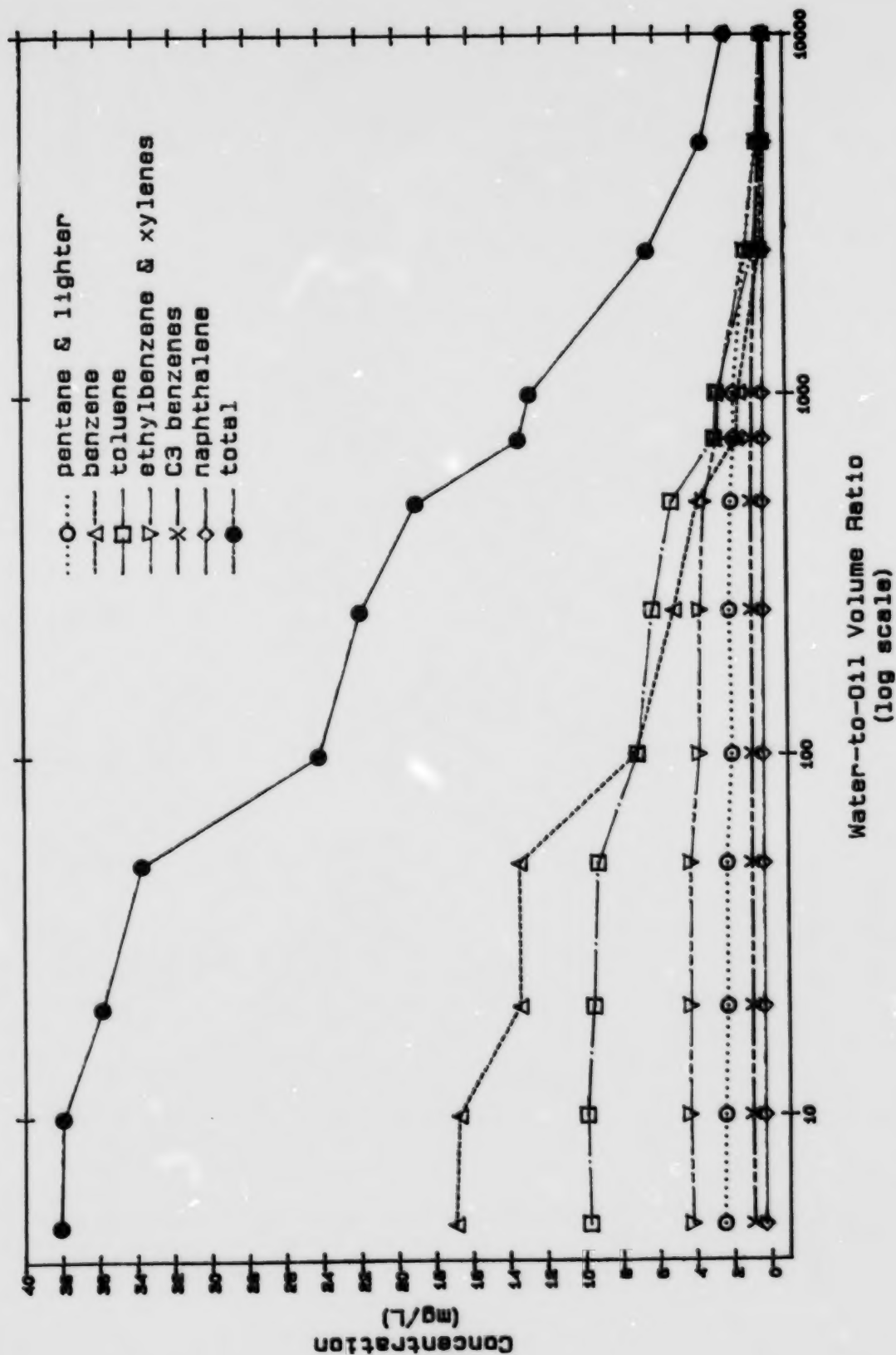


Figure 4: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Regular Unleaded Gasoline

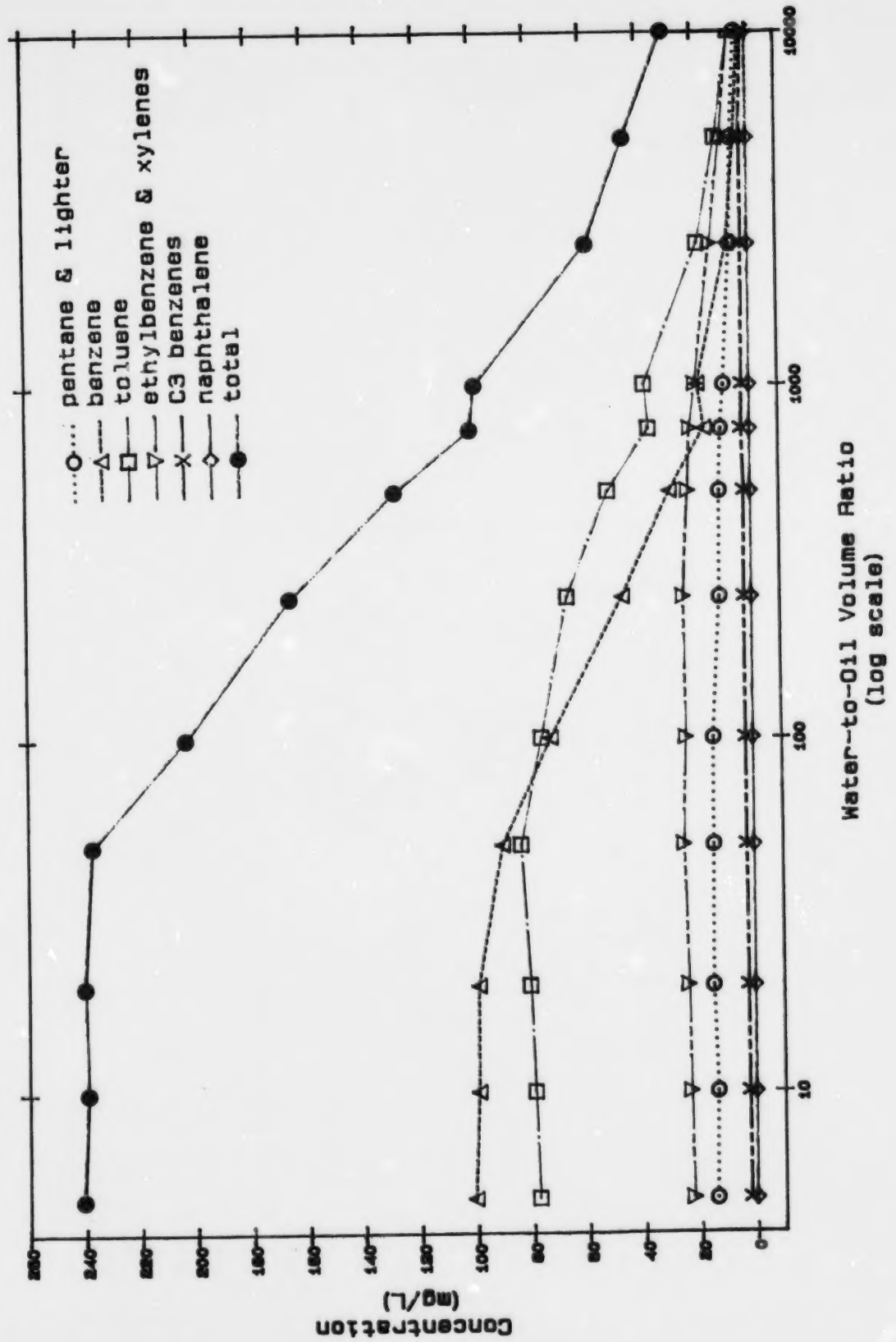


Figure 5 shows the dissolution behaviour of Bunker C Fuel Oil. The WSF's of Bunker C lack the presence of volatile aromatics which were predominant in the WSF's of the crude oils and gasoline. These WSF's contain a larger number of compounds and a large portion of less-soluble, non-volatile compounds.

Figure 6 presents the solubility behaviour of Fuel Oil No.2. The total concentration shows a dramatic change as the water-to-oil ratio is increased, this is especially true at low ratios of less than 100. This dependence is primarily due to the large concentration of pentane and lighter molecular weight compounds present in the WSF at these low water-to-oil ratios, but which dramatically decreases as the ratio is increased. The WSF's of the fuel oil contains significantly more compounds than those of crude oils and gasoline, and has a relatively high portion of non-volatile compounds.

Total WSF concentration as a function of water-to-oil ratio for the six oils tested are presented in Figure 7.

The results show that the water-to-oil volume ratio used during oil and water equilibration can significantly influence the concentration and composition of the WSF produced. The general dissolution behaviour that emerges is that at low water-to-oil ratios, the more soluble compounds present in the oil are the predominant components of the WSF which makes the total WSF concentration relatively high. As the water-to-oil ratio increases, the concentration of these compounds and the total WSF concentration decreases, and the less soluble compounds in the oil make up a larger portion of the WSF. Maijanen et al. (1984) described this behaviour as a "depletion effect"; the oil becomes depleted of water soluble material as the water-to-oil ratio is increased thus causing the apparent "solubility" to fall.

Calculated oil-water partition coefficients for selected hydrocarbons are presented in Table 1. The form of the equation fitted to the experimental data was that proposed by Shiu et al (1988). This theoretical equation based upon a simplified mass balance predicts that the concentration of any individual component in the water phase will be:

$$C_w = \frac{C_{wo}}{1 + (Q/K)}$$

where: K is the oil-water partition coefficient

Q is the water-to-oil volume ratio

C_{wo} is the concentration of the component in the water phase at $Q = 0$

C_{wo} was determined by extrapolating the concentration to a water-to-oil ratio of 0. All fitted functions obtained correlation coefficient (multiple R^2) values of at least 0.985.

The oil-water partition coefficients presented in Table 1 provide a numerical indication of the sensitivity of water soluble components to the water-to-oil ratio. From the equation $C_w = C_{wo} / (1+(Q/K))$, it can be seen that when the water-to-oil ratio (Q) equals the partition coefficient (K), the concentration of that component will be half of the value of C_{wo} . Therefore, components with low partition coefficients are most sensitive to the water-to-oil ratio. The calculated values in Table 1 also show that partition coefficients are extremely dependent upon the oil matrix. How an individual compound partitions itself between the oil and water phases will depend upon its concentration in the oil and its interactions with other solutes in both the oil and water phases.

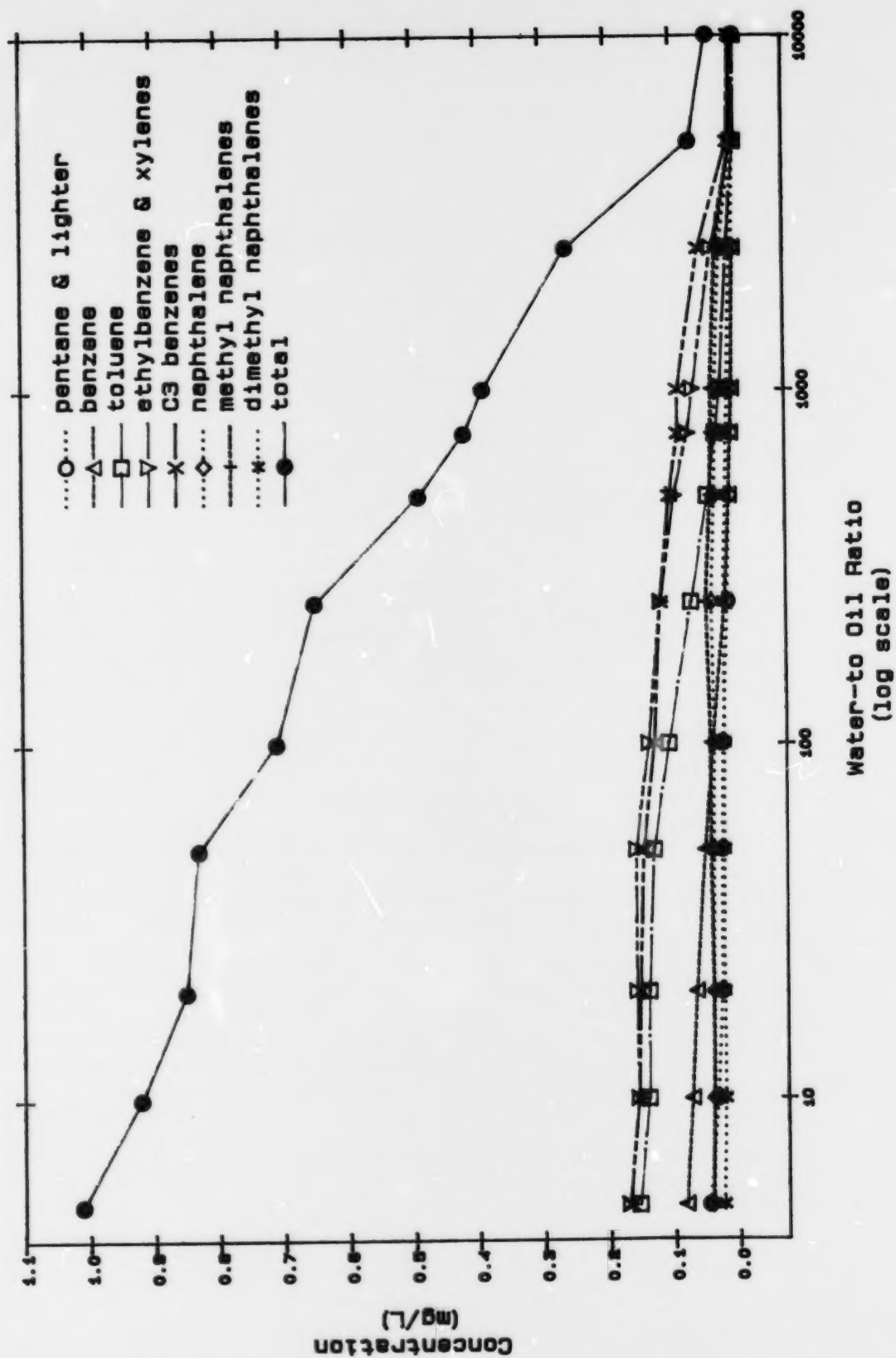


Figure 7: Concentration of Water-Soluble-Fractions versus Water-to-Oil Ratio

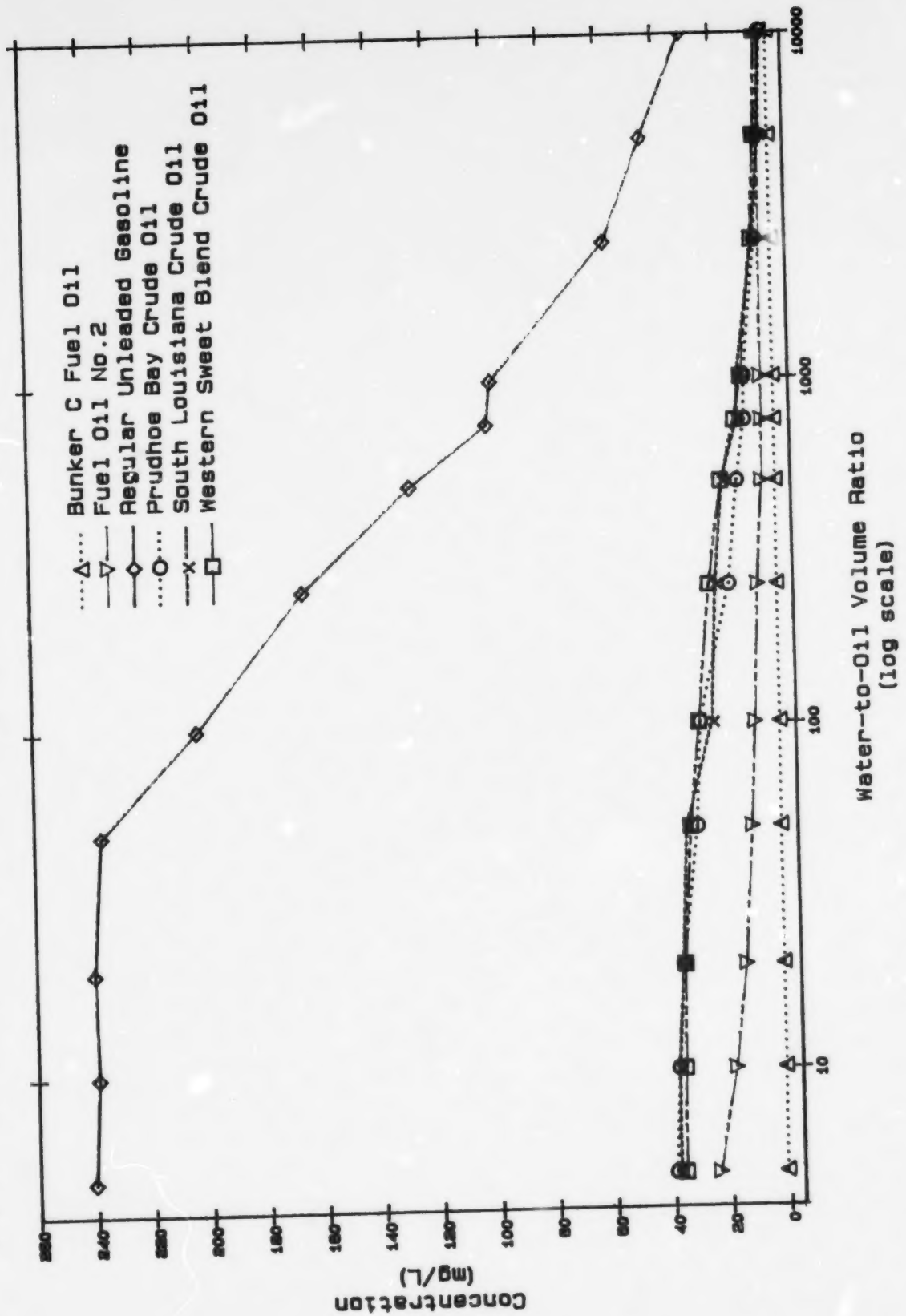


Table 1:

Oil-water partition coefficients

Component	Western Sweet Blend crude	South Louisiana crude	Prudhoe Bay crude	Gasoline	Fuel Oil No. 6	Fuel Oil No. 2
pentane & lighter	1,883	1,556	1,043	2,420	48	11
benzene	121	106	75	228	72	80
toluene	386	382	249	934	207	161
ethyl benzene & xylenes	1,105	1,248	895	4,758	568	524
C ₃ benzenes	3,707	3,548	3,313	62,000	801	2,509
naphthalene	2,126	1,975	1,947	162,600	1,178	2,319
methyl naphthalenes					3,930	5,160
dimethyl naphthalenes					7,716	42,351

Table 2:

Component Analysis of Oils
(mg/L)

Component	Western Sweet Blend crude	South Louisiana crude	Prudhoe Bay crude	Gasoline	Fuel Oil No. 6	Fuel Oil No. 2
pentane & lighter	24,750	28,730	12,520	203,520	2	214
benzene	2,600	3,360	2,860	23,960	6	60
toluene	6,130	6,640	6,260	63,520	32	480
ethyl benzene & xylenes	13,420	13,270	9,210	61,610	97	3,770
C ₃ benzenes				32	437	5,050
naphthalene	1,090	2,020	1,070		7,290	23,210
methyl naphthalenes					11,950	26,640
dimethyl naphthalenes						

One implication of WSF dependence on the water-to-oil ratio is that bioassay and solubility results obtained by researchers using different ratios may not be comparable. A review of the literature showed that water-to-oil ratios used for bioassay testing varied from 6:1 to 10,000:1. Also, it was not uncommon to find terminology in the literature that referred to "saturated" WSF solutions which were produced when an "excess" of oil was contacted with water. The definition of "excess" varied from researcher to researcher and with time. Recently, an "excess" of oil has meant a water-to-oil ratio of 20:1 or less. Our results show this assumption may not hold for all petroleum mixtures. The results for Fuel Oil No.2, presented in Figure 6, show that the WSF concentration is particularly sensitive to the water-to-oil ratio in this range. The fuel oil contains a low concentration of material with a relatively high solubility (pentane and more volatile hydrocarbons). The aqueous concentration of these highly soluble compounds drops from 14 ppm to 4 ppm when the water-to-oil ratio is increased from 5:1 to 20:1 and as a result, the apparent "solubility" of the oil drops by 10 ppm.

As noted by Shiu et al. (1988) and Lockhart et al. (1984), the effect of water-to-oil ratio on WSF's must be taken into account when extrapolating bioassay results to environmental conditions. The water-to-oil ratios in most spill situations would likely be several order of magnitudes larger than the those used in bioassays. Since the relative proportions of the individual components of the WSF vary with the water-to-oil ratio and each component has a different toxicity, the use of a dilution factor is unlikely to produce compatible results. The use of high water-to-oil ratios during oil/water contacting would produce WSF's more similar to those found in the environment.

The vessel used for oil/water contacting in this study was a closed system, thus loss of compounds by evaporation was prevented. In an open system such as a marine oil spill, volatile compounds would quickly evaporate. However, there are several real spill scenarios which could be considered "closed" to evaporation. Examples of a situation where little or no evaporation takes place are: when an oil spill occurs under ice cover; when petroleum from a leaking underground storage tank contaminates ground water; and when oil and water pass through processing units such as a separator or slop tank. The results obtained in this study could provide an indication of the dissolution behaviour of oils in these circumstances.

CONCLUSIONS

The water-to-oil volume ratio used during oil/water contacting can have a significant influence upon the composition and concentration of the water soluble fraction. This influence of the water-to-oil ratio upon the dissolution of oils must be taken into account if results from laboratory tests are to be indicative of environmental behaviour. The results show that the more soluble components of oil make up a large fraction of the WSF's composition at low water-to-oil ratios. At high water-to-oil ratios, these compounds become less significant and the less soluble compounds constitute a larger portion of the WSF.

The data from this study show that the three crude oils yield WSF's that are very similar in terms of both composition and concentration with slight differences in the relative abundance of some compounds. Gasoline was the most soluble petroleum mixture studied; its WSF's were enriched with benzene, toluene, ethylbenzene and xylenes. Compared to the WSF's of the crude oils and gasoline, the WSF's of the fuel oils lacked the presence of volatile aromatics but they were comprised of a relatively large number of less volatile, less soluble compounds such as tri-methyl benzenes, propyl benzenes, naphthalene, and alkylated naphthalenes.

ACKNOWLEDGEMENTS

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AN EXPERIMENTAL STUDY OF LARGE BUBBLE DYNAMICS

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INTRODUCTION

The overall behaviour of a bubble plume rising from an undersea oil well blowout is believed to be heavily influenced by phenomena very near the wellhead. The behaviour of such a blowout is immediately that of a plume rather than a jet due to the very rapid shattering of large bubbles into many small bubbles (Rowe and Topham, 1982). Large bubble dynamics must be investigated in order to furnish lower boundary conditions for bubble plume models (e.g. Rowe, Poon and Laureshen, 1989). The formation, departure and subsequent shape change of the large bubbles obviously causes motion in the surrounding liquid. A prediction of liquid velocities in the vicinity of the wellhead is vital to the design and positioning of devices to cap or contain the blowout (e.g. Brown and Root, 1985).

This paper describes experiments on the formation of large gas bubbles from submerged pipes. The bubble growth, departure and subsequent shattering is being recorded photographically for pipe diameters from 2.5cm to 10cm and gas flowrates up to 50 l/s. The results obtained to date and a discussion of the flow regimes observed and mechanisms believed to be involved are presented in this paper. Progress on an accompanying numerical model is also updated.

LARGE BUBBLE TEST FACILITY

The large bubble dynamics test facility consists of a 1.2m x 1.2m x 1.2m Plexiglass tank with an air injection system centred on the floor. The air injection system can be fitted with pipes of various lengths and diameters without draining the tank. It uses a small plenum chamber and perforated plates to provide axisymmetric velocity profiles in the test pipes (Rowe and Bugg, 1988). Air flowrate is measured with a circular arc, critical venturi flowmeter. In order to ensure choked conditions in the flowmeter, and cover the range required, two throat sizes are required. The water depth for all tests was 1.00m.

When the apparatus was completed and first tested it performed quite well and appeared to produce repeatable bubbles. However, there were initial problems with spillage from the tank, especially at high gas flowrates. Even at lower gas flowrates a large scale sloshing would slowly build in the tank and cause spillage. To counter this, a simple baffle system was designed and installed. This was very effective in limiting the spillage problems and the apparatus can now be run indefinitely with no large scale sloshing.

Commissioning of the test facility quickly indicated the realistic capabilities of the tank and air supply system. It was decided that test pipe diameters of 25.4, 50.8, 76.2 and 101.6 mm and gas flowrates from 5 to 50 litres/sec would be investigated. Although there are most certainly some small wall effects, the current tank is adequate to learn a great deal.

PHOTOGRAPHIC TECHNIQUES

A standard video system with a framing rate of 30 frames/sec was used to take the initial pictures. Because of the speed of the bubble movement, picture quality does suffer from blurring somewhat. However, most of the larger features of the bubbles are resolved quite well with serious blurring being restricted to the small bubbles created upon break-up. Although blurring is not a significant problem, the relatively slow framing rate quite often misses significant parts of the bubble growth process. This is particularly true for small pipe diameters with high gas flowrates. However, for most conditions it is possible to get such data as average bubble departure frequency from counting the bubbles formed during a known time period. This is certainly impossible from visual observations.

To give a higher quality picture of bubble growth and departure, a series of black and white 35 mm pictures of the pipe exit were taken under various conditions. At present no triggering mechanism has been implemented that would fix the time of the exposures in relation to each other. However, much can be learned from the still photographs because they give a much clearer picture than the video system owing to the higher shutter speeds attainable and the resolution of the media. Figure 1 indicates the conditions under which videos and still photographs have been taken as well as the extent of the run matrix.

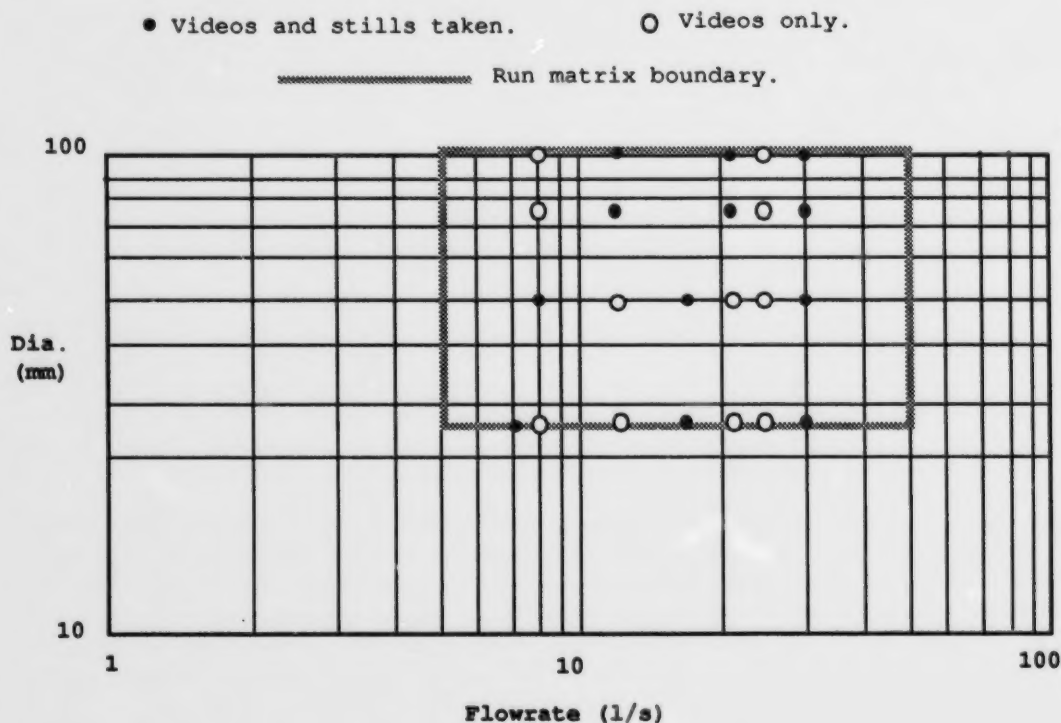


Figure 1: Run matrix coverage by video and still photography.

OBSERVATIONS

Since these data were only recently obtained, no detailed quantitative analysis has yet been accomplished. However, several interesting features of large bubble formation were immediately obvious. Still photographs will be used as illustrations, but the sequences were generally obtained by viewing the videos frame by frame.

Total Backflooding

For large diameter pipes at low gas flowrates there is often such significant backflooding that no large bubbles are formed. This is a lower bound that is of interest. This regime is most evident for the largest diameter pipe. Figure 2 shows the 101.6mm diameter pipe with a gas flowrate of 12.5 litres/sec. No bubbles are formed at the actual pipe exit. Much smaller bubbles, probably formed at the perforated plate on the floor of the tank, rise through the flooded test pipe. As the gas flowrate is increased there is no definite point where bubbles begin to form at the actual test pipe exit. At first, only occasional, small diameter toroidal bubbles form around the lip of the pipe. As the flowrate is further increased this becomes more common until it is the norm. At this stage there is still very significant backflooding down the centreline of the pipe but the pipe exit itself has become a definite site of bubble formation.



Figure 2: Total backflooding in a large pipe at a low gas flowrate (101.6mm, 12.5 l/sec).

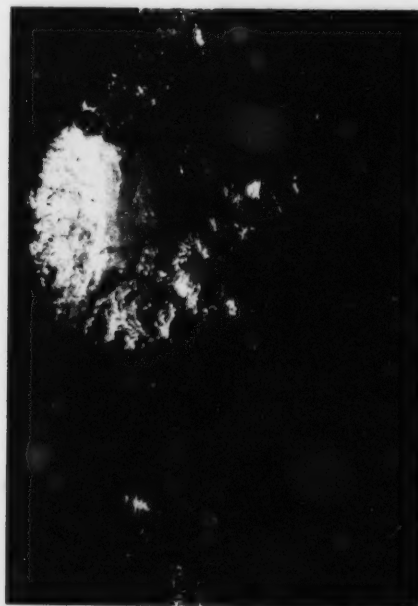


Figure 3: Initial growth stages of the first bubble in a typical pair (76.2mm, 30 l/sec).

Single Bubbles

Over quite a narrow range of conditions, single bubbles are formed. However, in most cases the transition between severe backflooding and multiple bubble formation does not include a definite region where single bubbles are produced.

Pairing

Over a very large range of the above run matrix there is a definite pairing of bubbles taking place. This process involves two different types of bubbles being formed. The first type of bubble has a quite spherical upper surface and appears to be relatively unaffected by the previous bubble formed. Figure 3 shows a good example of the initial growth stage of the first bubble of a typical pair. Note the relatively smooth surface and regular shape at this stage. As it rises large deformations in its surface begin to grow. A more mature bubble is shown in figure 4 where the surface has become quite irregular. After departure of the first type of bubble, the second type begins to grow. As this bubble grows, its top surface points upwards toward the rear of the first bubble as shown in figure 5. It appears to be quite heavily influenced by the flow field around the first bubble. As it departs it accelerates very rapidly upwards and is stretched along the vertical axis. It very quickly collides with the first bubble and seems to trigger complete break-up.

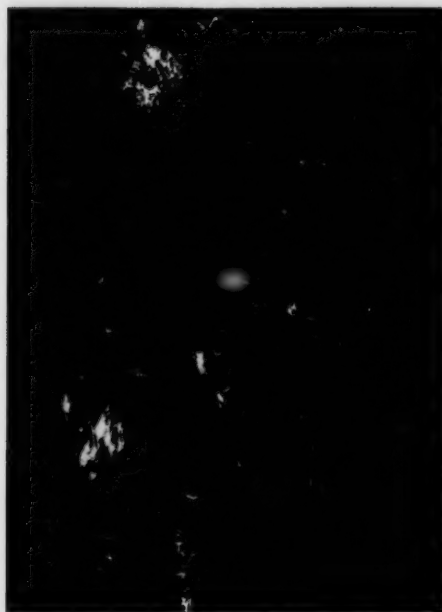


Figure 4: Later growth stages of the first bubble in a typical pair (76.2mm, 30 l/sec).



Figure 5: Second bubble of a typical pair elongating to penetrate first bubble (76.2mm, 30 l/sec).

Larger Groups

Multiple bubble formations in groups greater than two are also observed on occasion. Sequences of three bubbles are quite common and sequences of four or five also occur. An example of a group of three bubbles can be seen in figure 6. The first bubble is the largest and has an extremely rough surface. The second bubble is just penetrating the bottom of the first and displays the large amount of stretching along the vertical axis that takes place during such a penetration. The third bubble is just about to depart and is extending upwards to penetrate the second one.

Chains

For the small pipes at high flowrates no real groups occur. Each bubble seems heavily influenced by the previous one and is literally pulled from the pipe by the circulation of the previous bubble. As each bubble departs it is stretched about the vertical axis of the pipe a great deal. An example of a high gas flowrate through a small diameter pipe is shown in figure 7. Here, almost every bubble formed is influenced by the previous one and a continuous train of vertically elongated bubbles dominates the region just above the pipe exit.



Figure 6: A group of three interacting bubbles (50.8mm, 17 l/sec).



Figure 7: Multiple bubble formation in large groups (25.4mm, 30 l/sec).

No Backflooding

The upper bound of backflooding appears to be at quite a high flowrate. The only cases where there is definitely no backflooding is the 25.4mm diameter pipe at all gas flowrates tested and the 50.8mm diameter pipe at gas flowrates above 25.5 litres/sec. Figure 7 shows a complete lack of backflooding into the pipe. From the pictures presented here it is obvious that a large range of operating conditions have some degree of backflooding even when quite large bubbles are being formed. This backflooding appears primarily down the centreline of the pipe; see, for example, figure 3 where a column of liquid along the centreline of the pipe can be seen through the bubble.

Flow Regime Map

The preliminary observations described above can be used to construct a flow regime map that illustrates bubble behaviour at the pipe exit. The boundaries indicated on this map are very approximate due to the sparse cover-

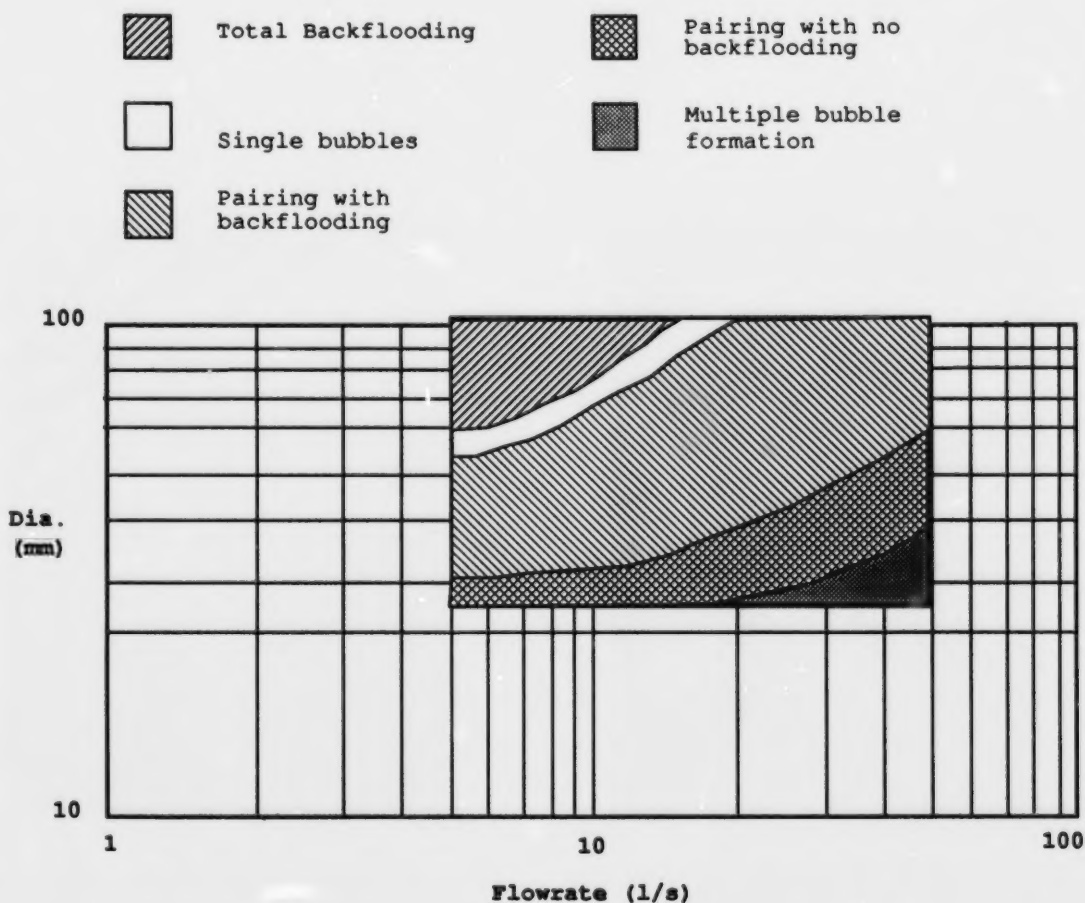


Figure 8: Flow regime map for large bubbles formed at submerged pipe exits.

age of the run matrix to date and the gradual change in behaviour observed as the main parameters were varied

Only the major regimes are shown on this map and they consist of combinations of the phenomena just described. The first is the total backflooding regime dominating the upper left region of the flow regime map. In the next regime the formation of single large bubbles is dominant. In this regime a very large amount of backflooding is still observed but single large bubbles with little influence on one another are formed. As the flowrate is increased pairing becomes dominant. This is the largest regime observed. Most of the pairing regime also involved significant backflooding. However, some conditions exist where pairing occurs with no backflooding. This regime is also indicated in figure 8. The last regime on the map is that of multiple bubble formation where chains of bubbles that are heavily influenced by the previous bubble are dominant. No backflooding was observed in conjunction with this regime.

Bursting

Another process observed on the videos is that of bursting. Because of the large size of the bubbles generated they are very unstable and soon burst into groups of small bubbles. This bursting apparently takes place by a rapid growth of disturbances in the bubble's surface which, because of the large size of the bubble, cannot be damped by surface tension. Also, the penetration of a tongue of liquid from below, to be discussed shortly, plays a role. When multiple bubble formation is taking place, the group of small bubbles formed will consist of gas from a series of large bubbles which have combined as described earlier. Since the formation of large bubbles at the orifice is intermittent, the bursting creates periodic groups of small bubbles which rise to the surface as a buoyant plume. The behaviour of groups of bubbles in a buoyant plume is being considered by another graduate student in a related study (see Laureshen and Rowe, 1989).

MODELLING

The effort to numerically model the growth of large bubbles at the exit of large pipes is progressing in parallel with the experiments just described. Briefly, the numerical model solves a two-dimensional discretised form of the Navier-Stokes equations on a cartesian or axisymmetric finite difference grid. Much work has been done on the sudden release of single cylindrical and spherical bubbles into a quiescent fluid. This work is described in Bugg and Rowe (1989) and models experiments performed by Walters and Davidson (1962) and (1963). It has been found to be very successful in predicting the rise velocity and shape change of large isolated bubbles.

Although the problem of single bubbles is much simpler than the phenomena being studied in the experiments, the fundamental behaviour of these bubbles has important features in common with large bubbles formed at an orifice. When a large bubble is released and begins to rise, the dominant change that takes place is the penetration of a tongue of liquid into the bottom of the bubble. This liquid soon contacts the top surface causing the break-up of the bubble into a small spherical cap and a large toroid (see Walters and Davidson, 1963). This shape change generates a large amount of circulation in the flow as it transforms from irrotational flow around a sphere to the highly rotational flow of a rising ring vortex. This circulation cre-

ates very large upward velocities along the axis of the bubble. This phenomena appears to contribute heavily to many of the observations discussed above. The penetration of a tongue of liquid from below is difficult to see during continuous gas injection. However, very large, periodic, upward velocities along the axis of the pipe were certainly observed. Also, the phenomena of pairing and multiple bubble formations seems to be explained by the presence of a ring vortex associated with a previously departed bubble. If the gas flowrate is high enough that the second bubble of a pair is formed before the ring vortex has risen very high, the liquid velocities associated with the ring vortex elongate the second bubble upwards and pull it into the first bubble. This accelerated departure of the second bubble allows a larger space to occur between it and the next pair, thus allowing the next bubble to grow with little influence from the circulation of previous bubbles.

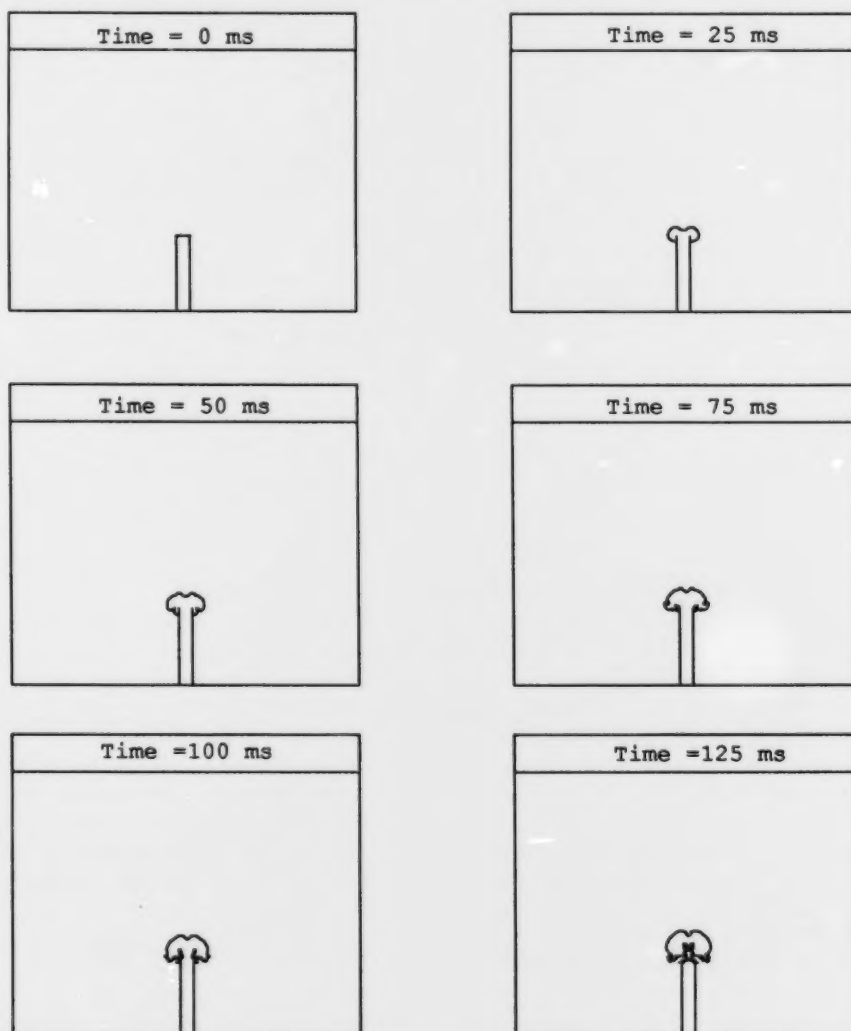


Figure 9: Model results for constant mass flow of 0.02 kg/sec from a 50.8mm diameter submerged pipe.

The model is currently being applied to the problem of gas escaping from a submerged pipe. A preliminary run showing a constant mass flow of 0.02 kg/sec escaping from a 50.8 mm diameter pipe is shown in figure 9. This shows several features observed in the experiments. The initial stages of growth appear as a toroid attached to the rim of the pipe much the same as shown in figure 3. To date the simulation has progressed just to the point of departure but work is ongoing to extend the numerical model to multiple bubble formation.

CONCLUSIONS

It is clear from the observations described in this paper that much can be learned by studying bubble processes within the capabilities of the present apparatus. The photographs taken so far show incredibly complex phenomena occurring within just a few diameters of the pipe exit. It appears that the run matrix is capable of exhibiting several different flow regimes. These include total backflooding, where the large diameter pipe is not even the site for bubble formation, single intermittent bubble formation, groups of two or more bubbles and chains of many bubbles influenced significantly by each other. For at least the two smallest pipes (25.4mm and 50.8mm) the test rig is capable of flowrates which eliminate backflooding.

The intermittent production of small bubble groups due to the shattering of large bubbles is observed in the laboratory. These groups of small bubbles are not necessarily produced at the same frequency as large bubbles are expelled since the large bubbles were observed to form pairs over a wide range of conditions. These observations support the hypothesis of a blowout behaving like an intermittent buoyant plume under some conditions.

A very large intermittent vertical velocity along the centreline of the pipe is also observed. This could be due to ring vortices formed by the shape change of previously expelled large bubbles. The very high velocities observed in the preliminary experiments point to extremely large dynamic forces on any capping or containment device brought into the vicinity of a subsea blowout.

It is clear that producing a full scale blowout in the laboratory is well beyond the capabilities of all but a very ambitious and heavily funded experimental program. However, if the numerical model can be demonstrated to yield reasonable results for the experiments described in this paper, it can be economically extended to the conditions of an actual blowout. Thus far it has provided predictions of the shape change of single isolated bubbles released in a quiescent fluid that compare very well with experimental results. On the problem of continuous flow from a submerged pipe, initial results are promising.

ACKNOWLEDGEMENTS

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PHYSICAL AND CHEMICAL PROPERTIES OF SPILLED OIL

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ABSTRACT

A laboratory-scale study of an oil spill is a useful and often the only way of obtaining necessary information required for mathematical modelling of spill spreading and fate, for contingency planning, environmental impact assessment, etc. In order to estimate the reliability of the laboratory investigations, data collected at a spill of opportunity should be used to verify laboratory results whenever possible. A spill of about 35,000 tons of oil occurred in 1980 in the Gulf of Guinea and a sequence of various studies has been conducted during and after the spill. Some of these results are revealed in this paper. They are relevant to laboratory study of the weathering process of commercial crude oils in standard Mackay's apparatus. Rheological properties of oil-water emulsion and aerated oil have been studied as well. The intent of this work was to obtain laboratory results which could be compared with the open water oil spill data and also to develop a fundamental understanding of the rheology of weathered crude oils.

INTRODUCTION

Crude oil exposed to the surface of water undergoes several physical and chemical processes, which can diminish the volume and alter the composition of the oil. An oil spill is exposed to several complex and interrelated processes: evaporation, emulsification, dissolution, biochemical degradation, sedimentation, and sinking. According to Parker, Freegarde, and Hatchard (1971), spreading of oil released on water is the most important process for the first ten hours following a spill. At the same time, evaporation will take place (20-30 percent of hydrocarbons in 2-3 days) so that the oil remaining becomes increasingly richer in the less volatile components and so more viscous.

Crude oil is weathered over time by the interactions with environmental parameters and system fluxes to produce changes in physical and chemical properties. Generally, the lower boiling components are evaporated and the remaining pollutant is simultaneously emulsified with the water and exposed to other weathering processes. The rate at which the various hydrocarbons in the petroleum are affected depends upon their structure and molecular weight. Ambient conditions, such as temperature, wind and sea state can control the rate at which the processes occur. The rate of evaporation at atmospheric pressure depends largely on the vapor pressure of the oil. High winds, rough weather and increased surface area enhances the evaporation process. Crude oil exposed to evaporation can produce noticeable property changes within minutes, though hours, weeks and months are required to detect the changes induced by oxidation, dissolution and biological attack.

When the slick thickness goes below 8 mm, gravity no longer influences the oil's diffusive forces, and viscosity of the film will begin to control the oil's behavior. Finally, thin film of oil will be formed in which the relatively small interfacial tension at the edge of the slick will be the dominant

spreading force. The size and thickness of an oil slick in an instantaneous spill depends on its discharge volume. Another important property of oil which affects the slick size and thickness is density. As a rule, heavier crudes will spread less than the lighter ones. The slick thickness is proportional to oil density.

Evaporation occurs at the immediate moment of a spill; the rate of which decreases exponentially. Light, volatile hydrocarbons evaporate within 24-48 hours and, in general, pentadecane is the lowest normal alkane usually found in the weathered oil. These more volatile components make up 20-50 % of most crude oils. The remaining oil typically has higher values than the original material for properties such as relative density, viscosity, wax, asphaltene, temperature for a given distillate yield, pour point, flash point, carbon residue, sulphur, and metal content. Fuel oil, lubricating oil and tars, lacking the volatile components found in crude oil and gasolines, evaporate far less quickly.

The viscosity of crude oil predominantly controls the rate of oil spreading in the first few hours of a spill, but undergoes a rapid and continuous change in influencing the lateral spreading of oil on a water surface. A typical crude exhibits a transition from Newtonian to non-Newtonian behavior following the weathering process. Also emulsion formation is associated with changes in oil's rheological properties. Crude oil, as it is produced from the geological formations, can readily form water-in-oil emulsion or "chocolate mousse". Literature reviews on this subject are available in Mackay and Zagorski (1982), Payne and Philips (1985), and Ross (1986).

Similar emulsions are also frequently formed in accidental spills on water under natural environmental conditions. With most oils, the surface tension of the oil is less than that of water, so that wind and wave action on the oil will favor the water-in-oil type. Where the surface tension of oil is greater than the surface tension of the water, the oil disperses in μm -sized droplets into the water and conditions will favor oil-in-water emulsions. Also, in the presence of inorganic polyatomic ions under various conditions, water-in-oil emulsions can change into oil-in-water emulsions. The emulsions are probably stabilized by colloidal particles (e.g. asphaltene and waxes) which are placed at the w/o interface where they may form a stable film of considerable mechanical and elastic strength around the water droplets (Daling and Brandvik, 1988). A stable water-in-oil emulsion may contain up to 80 per cent water. The volume of emulsion is often appreciably greater than the volume of oil spilled. The viscosity of the emulsion is always higher than that of its oil component, such that they can appear to be solids or semi-solids.

EXPERIMENTAL

Compositional changes of crude oils due to physical-chemical weathering have been documented in both field and laboratory studies. This paper reports results of a field studies conducted during blowout of the Funiwa 5 production well which occurred on January 17, 1980, in the Gulf of Guinea, offshore Rivers State of Nigeria. An estimated 35,000 metric tons of light crude oil was released in the period of almost three weeks. The magnitude of the spill was that of the Ekofisk blowout (April, 1977) and it was much larger than the Santa Barbara blowout. Lack of publicity and spill data for the Funiwa 5 blowout make the record of the history of oil spills incomplete. Only very scarce data on this blowout can be found in the literature (Baker, 1981; Ekekwe, 1983; Palczynski, 1984). Accessibility for control, availability of marine science

laboratories with experienced and skilled staff, public awareness, and availability of funds are main factors affecting the extent of oil spill research and impact assessment. There are two important features which make the Funiwa 5 blowout unique, namely a large quantity of oil was released in a short time (over two weeks) and the location of the spill in the tropical, ecologically rich and sensitive environment. The predominant movement of oil was inland to the Niger Delta and along the coast due to tide, current and wind action. Numerous samples of crude oil, polluted fresh and sea waters, oiled sand, and plants were collected in the area affected by the spill along the 40 km long coastal line (Fig. 1) and analyzed. Surface water was up to 3 mm deep and near the surface was up to 5 m. Crude oil samples were taken at different locations in creeks between 100 m and 300 m inshore; fresh crude was also available. All samples were stored in the dark and refrigerated until analyzed.

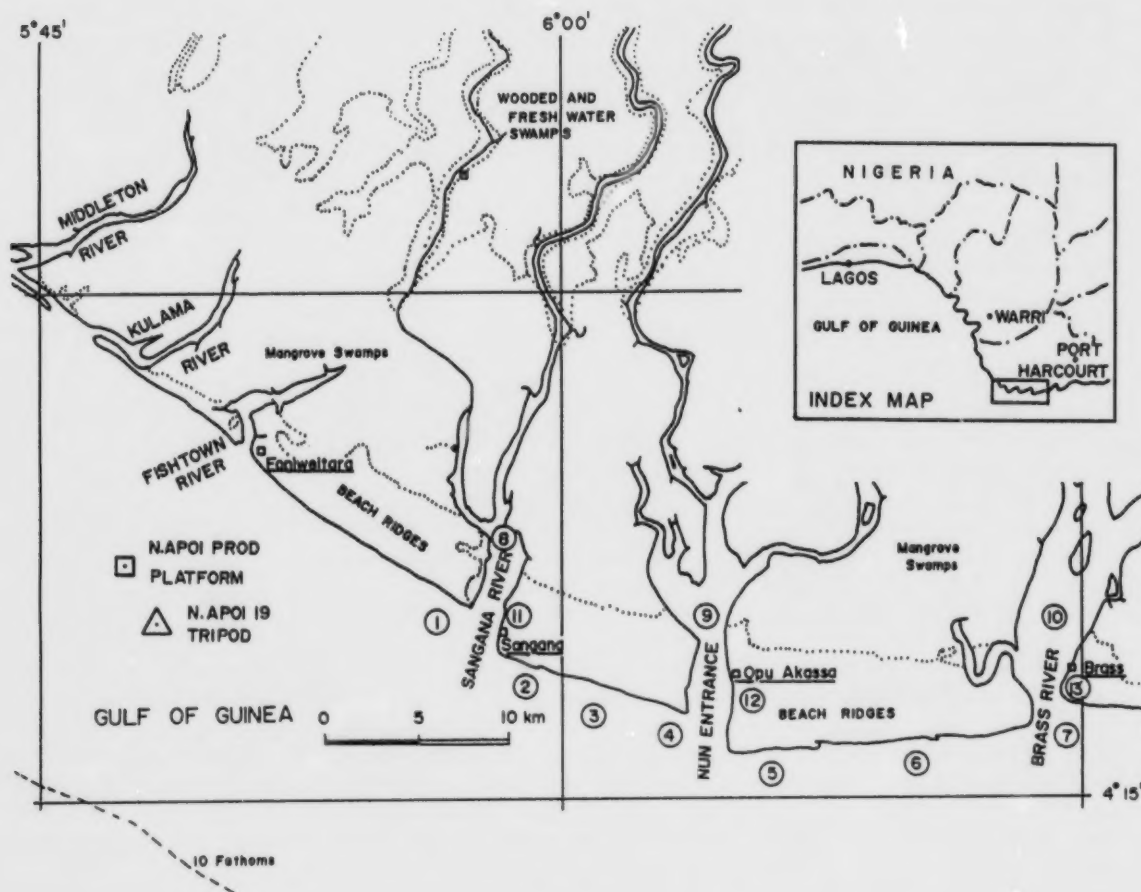


Figure 1. Map of the study area of the Rivers State of Nigeria showing location of the sampling stations.

Oil samples were analyzed for fractional composition, viscosity, specific gravity, water content, sulfur concentration, pour point, and surface tension according to ASTM standard analytical methods. Samples of water were tested for oil content (dissolved and dispersed) by centrifugation followed by extraction with chloroform to give a total content of oil as CCE value in mg L^{-1} . Chemical oxygen demand (COD) was found by a standard ASTM D1252 method. The Winkler method was used for determination of dissolved oxygen (DO).

In order to verify the field's study, a scale-down modelling of the weathering process of crude oils was performed in standard Mackay's apparatus. Measurements of rheological and other physical properties of oil during the process of weathering were taken. Mackay and Stiver (1982) have suggested several methods for weathering or artificially evaporating oil with the purpose of simulating natural evaporation. They estimated that 1 million volumes of air per one volume of oil simulate one day's weathering, and this approximation was adopted into this study. With the gas stripping method used in the project a known volume and mass of oil was charged in a measuring cylinder or flask fitted with a porous disc or tube through which air can be blown at a relatively slow, constant rate. The volume and mass of the oil was periodically measured. The air flow rate was measured by a gas meter or flowmeter. Flow rate of air was around 4 L/min and oil/water mass ratio was as 1:1 and a time of the experiment was up to 10 hours. A schematic of the weathering apparatus is shown in Fig. 2.

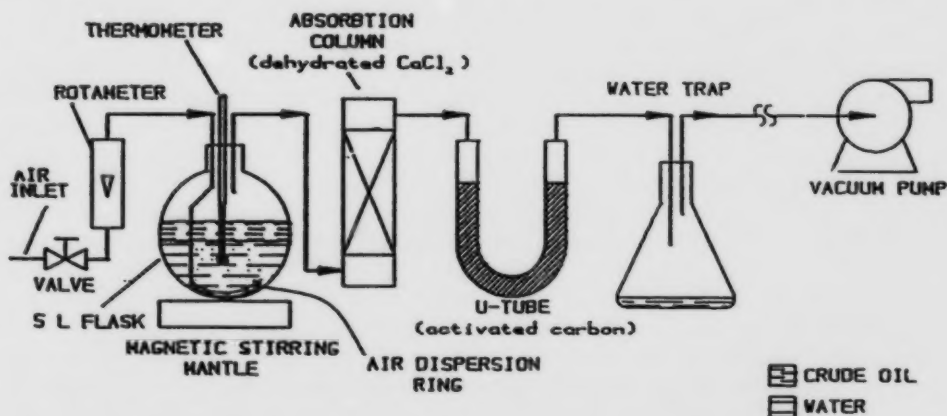


Figure 2. Schematic diagram of the weathering apparatus.

The addition of water to the flask made the relative volume measurements difficult because the two fluids emulsified. Volumetric oil and water content in the emulsion was identified after separating components with a centrifuge. The samples of oil were analyzed according to ASTM methods for fractional composition.

Oil-water emulsions for the study of rheological properties were formed in the process of one hour of intensive mixing with a metal stirrer at 100 rpm of predetermined masses of oil and sea water in a beaker at controlled temperature. Immediately after the stirrer was tuned off, the viscosity of emulsion was determined with the Brookfield Digital Viscometer Model DV-1. The viscometer rotates a sensing element in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement.

Continuous readout of viscosity was accomplished by means of the integral three-digit LED display and by a chart recorder into which the 0-10 mV analog viscometer output signal was transmitted. A cylindrical spindle was used with the viscometer. They are particularly valuable when measuring non-Newtonian fluids because their defined geometry facilitates mathematical analysis. Constant-temperature batch assured constant temperature measurements. The small sample adapter was used for samples of volume between 2.0 and 16.0 mL. This adapter measures viscosities from 5 cP to 10,000 cP at shear rates from 0.066 to 93.0 s⁻¹. The jacketed design permits connection to a circulating-type bath for temperature control.

RESULTS AND DISCUSSION

Crude oil is a complex mixture of hydrocarbons and non-hydrocarbons which commonly are classified into the following groups: saturated (e.g. alkanes and naphthenes), aromatics, NSO compounds and asphaltenes. Small differences in composition between different crudes can greatly affect the physical properties and hence the formation and stability of emulsions when oil is spilled on water. Furthermore, the composition of the crude is changed by weathering at sea.

It has been noticed during the Funiwa 5 spill that the amount of oil at sea decreased rapidly upon blowout termination due to the weathering process; however, the extent of the spill increased, which was confirmed by analyses of water samples collected along the coast. All results reported in this paper are the average value of at least three samples collected at the places indicated in Fig. 1. As shown in Table 1, concentration of chloroform-extractable hydrocarbons (CCE) and the chemical oxygen demand (COD) were higher in the surface sea water than in near-surface water. This was probably because oil is lighter than water and floated on the water surface at the time when samples were taken. It can be seen in the last column of Table 1 that surface concentration of oil changed dramatically from the maximum value of over 4 Lm⁻² (3 mm-thick slick) in the third day since the blowout started in nearshore water close to Sangana (station 1) to 0.26 Lm⁻² (0.1 mm thickness) in the 19th day and to 0.009 Lm⁻² (0.005 mm thickness) by February 13 and continued to decrease further. Concentration of hydrocarbons, in samples of the surface seawater, reached high values in the 19th day of the blowout to fall to lower values three weeks later. To compare with the International Fishery Water Quality Standard of less than 0.05 mgL⁻¹ for oil, the whole area should be considered as heavily polluted, especially in the third week of the spill with concentration of hydrocarbons toxic for many marine species. The content of dissolved oxygen (DO) in the surface water was lower in areas and at a time where a layer of oil covered water, inhibiting aeration. Decrease in the dissolved oxygen concentration could also be caused by the oxygen consumption due to the biochemical oxidation of the organic material. After some time, when the slick dispersed naturally, values of DO were quite similar in surface and subsurface waters, reaching the saturation condition which is 8.8 mg O₂L⁻¹ at 22°C and 7.9 mg O₂L⁻¹ at 28°C.

Specification of crude collected at different times after the blowout is given in Table 2. The specific gravity of spilled crude is greater than that of a fresh one and the oil viscosity also increases with the age of the slick, as illustrated in Fig. 3. It was revealed that with rise in the boiling point of oil, the ratio of viscosity of weathered oil to a fresh one increases, as shown

TABLE 1

Concentration of chloroform-extractable hydrocarbons, dissolvent oxygen and chemical oxygen demand in surface and near surface seawater.

Date (1980)	Days since blow out started	Sampling station	Concentration, $\mu\text{g L}^{-1}$						Surface conc., g m^{-2}
			Surface water			Subsurface water			
			CCE	DO	COD	CCE	DO	COD	
Jan. 20	3	1	145.2	1.7	363	2.5	3.1	16	4052.3
		2	94.9	2.0	202	1.0	3.6	9	690.5
		3	49.3	3.3	67	0.5	3.0	10	20.8
		4	0.2	4.8	13	0.3	4.6	8	0.0
		5	0.0	5.0	9	0.0	4.8	7	0.0
		6	0.0	5.2	5	0.0	4.5	6	0.0
		7	0.1	5.2	8	0.0	4.0	4	0.0
Feb. 5	19	1	145.7	0.6	195	2.2	5.0	9	263.9
		2	93.3	1.5	112	1.7	5.2	7	94.4
		3	130.8	0.7	233	0.9	3.5	22	130.0
		4	233.5	1.2	327	1.5	4.7	24	387.6
		5	25.0	2.0	100	1.9	5.8	17	91.2
		6	88.6	2.4	60	0.8	5.9	10	112.5
		7	53.6	2.3	54	0.8	5.5	5	43.3
Feb. 13	27	1	7.9	7.8	16	0.8	7.7	5	9.3
		2	10.7	6.6	32	3.4	7.3	37	32.0
		3	5.0	7.3	19	1.1	7.4	4	7.1
		4	4.3	7.1	14	0.5	8.1	5	23.8
		5	4.8	7.0	10	0.9	8.0	6	18.9
		6	8.2	6.9	29	1.3	7.0	22	0.7
		7	26.1	6.6	40	3.0	7.2	23	29.6
Feb. 25	39	1	0.2	7.0	6	0.2	7.9	8	0.5
		2	2.0	7.1	14	1.4	7.6	10	1.2
		3	1.3	7.4	7	0.9	7.8	7	0.0
		4	0.7	7.8	11	0.9	8.0	11	9.3
		5	0.4	7.6	5	0.3	8.1	6	0.0
		6	0.3	7.5	6	0.3	8.0	9	0.0
		7	0.4	7.5	6	0.5	8.1	8	13.2

in Fig. 4. As the film spreads, the rate of evaporation of the lighter components with the boiling point below about 300°C commences because of the increase in surface area, and the fractional composition of weathered crude changes. The sample of oil recovered on the 13th of February, i.e. two weeks after the blowout ceased, lost almost 20% of hydrocarbons and its boiling point increased from 63°C up to 280°C (Fig. 4). Prior to the fractional distillation, water was separated from oil by centrifuging. Evaporation of the volatile, lower molecular weight components and emulsification of oil, oxidation followed

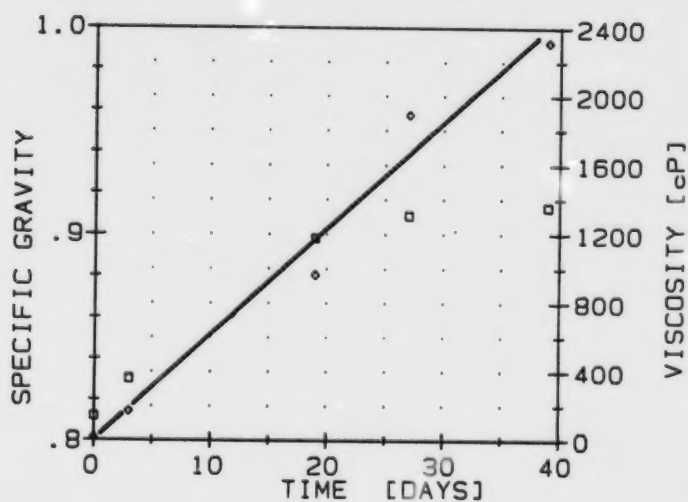


Figure 3. Specific gravity and dynamic viscosity of weathered oil, plotted against time days after the Funiwa 5 blowout started.

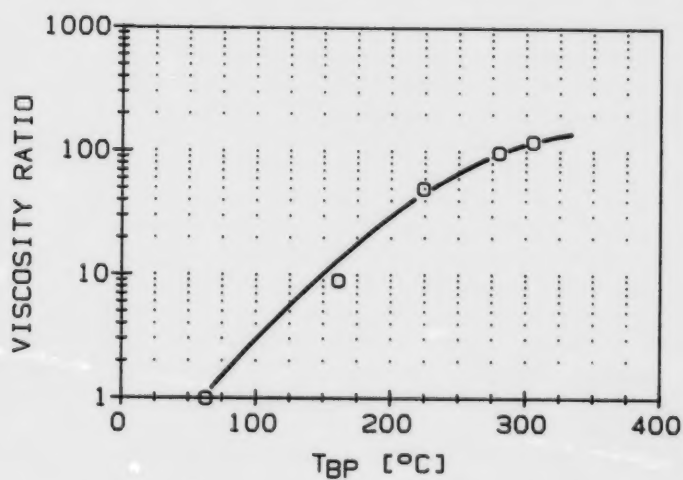


Figure 4. Ratio of viscosity of weathered oil to viscosity of fresh oil vs boiling point of weathered oil.

TABLE 2

Specification of crude oil recovered at Sangana river.

Date (1980)	Days since blow out started	Specific gravity	Concentration, % wt.			Dynamic viscosity, mPa s (38°C)	Pour point, °C	Initial boiling point, °C	Spreading coefficient, mN m ⁻¹ (30°C)
			oil	water	sulfur				
Fresh crude oil		0.812	n.a.	n.a.	0.25	19	-24	63	22.8
Jan. 20	3	0.830	75.6	22.1	0.22	173	7	161	3.1
Feb. 5	19	0.898	68.0	27.1	0.13	965	12	224	- 9.8
Feb. 13	27	0.909	48.1	40.5	0.09	1891	25	280	-15.6
Feb. 25	39	0.913	30.6	65.9	0.04	2316	27	305	-23.7
ASTM method		D1298	D95-62	D1551	D445	D97	D86-67	D971-50	

by microbial degradation, either aerobic or anaerobic, are the main factors responsible for viscosity increment. The rate of oil spreading and resultant thickness of the oil film varies with time. Depending upon the volume of the spill, after some interval, surface tension and viscosity forces become the principle determinants. If the resultant spreading force, represented by the Spreading Coefficient (SC), is positive, the oil will spread on water; if negative, it will not spread but will remain as a slick of liquid. The spreading coefficient is defined as surface tension of water phase minus surface tension of oil phase minus interfacial tension of oil/water. It appeared that oil up to few days old has positive SC, therefore would spread; weathered oil revealed a negative SC and will not spread. Samples of spilled oil taken at different times showed a large variation in the water content. A three-days-old oil sample contained 25% of water while the last sample, collected on the thirty ninth day since the blowout started, contained as much as 66% of water. It appeared that a relationship exists between water content and dynamic viscosity of the sample described by the equation: $Y = 3522 - 71656/X$, where X is the concentration of water in oil, in %, and Y is viscosity of the sample, in mPa s (or cP). The coefficient of determination for values listed in Table 5 is 0.990, which indicates good agreement between the calculated and the empirical values, as shown in Fig. 6.

Air stripping and emulsion formation in laboratory conditions were performed with the use of five brands of crude oil obtained from local refineries. Their properties are listed in Table 3. The table shows values of viscosity measured with the Cannon-Fenske capillary viscometer (CF) and with the Brookfield viscometer (DV-1).

Air stripping removes hydrocarbons of the high-vapor pressure (usually saturated aliphatics) and the fractional composition of oil changes. This is illustrated in Fig. 7 in which distillation curves for the Palanca and Brend oils before and after air stripping are shown. Distillation of oils was performed under atmospheric pressure until temperature reached 250°C. The boiling points were around 40°C, similar for all oil studied while fractional composition varied. Changes in the fractional composition follows with increase in viscosity and density of oil as illustrated in Figures 8 and 9.

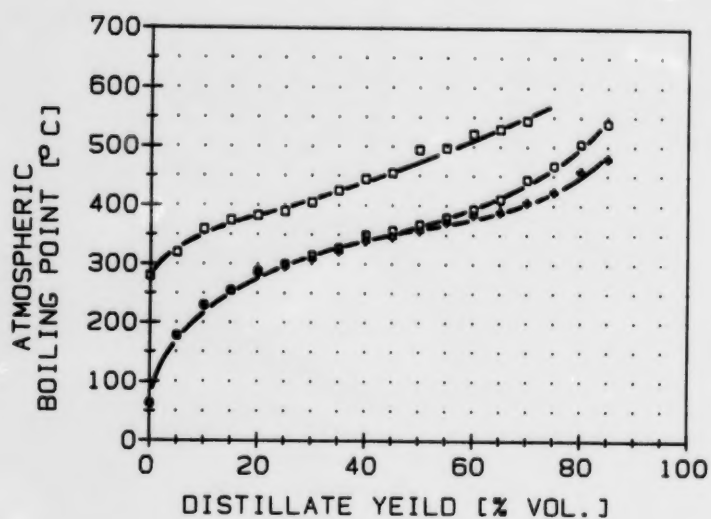


Figure 5. Distillation curves of Funiwa 5 (+) and Obigbo North (□) fresh crude and weathered Funiwa 5 (○) oil collected on February 13, 1980.

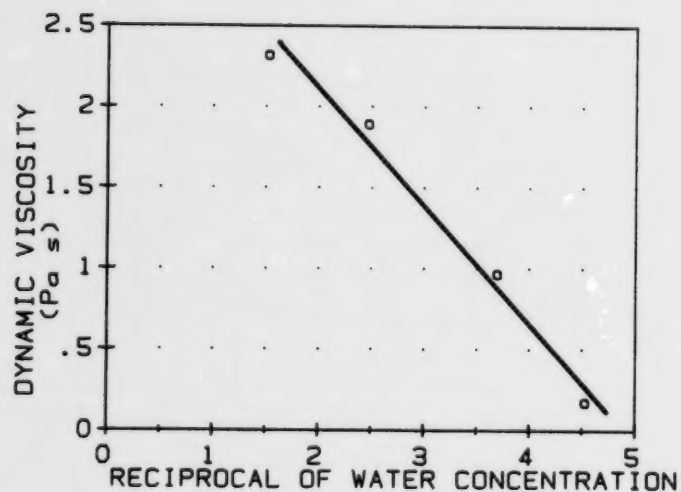


Figure 6. Effect of water content (reciprocal of water fraction in the sample) on the dynamic viscosity of the weathered oil.

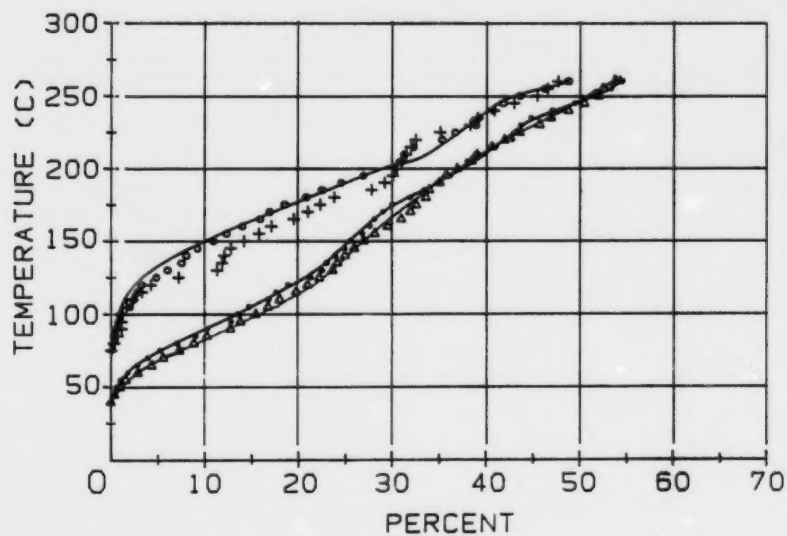


Figure 7. Distillation curves for the Palanca (Δ) and Brent ($\bullet$) oil before (lower line) and after (upper line) air stripping.

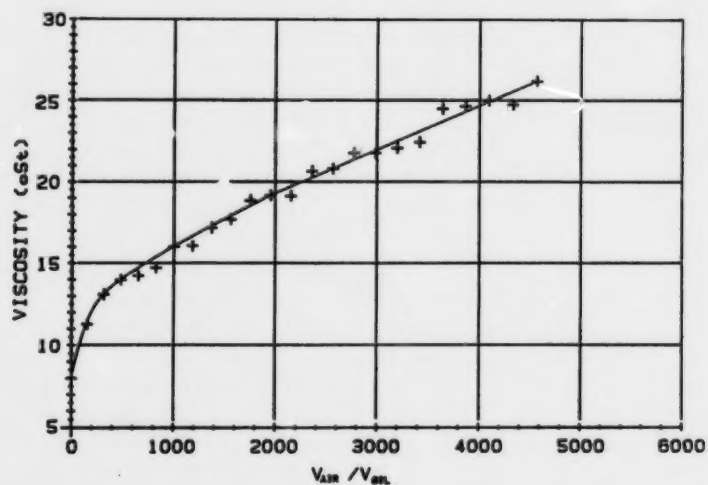


Figure 8. Viscosity change of the Floha oil as a result of the aeration process.

TABLE 3
Physical properties of crude oils.

Crude Brand	Density (kg/m ³)	Surface Tension (dyne/cm)		Viscosity (cP)		°API
		Air-Oil	Oil-Water	C-F	DV-1	
Palanca	829.3	29.2	19.7	4.45	5.04	39.0
Brent	829.7	28.6	14.1	4.31	5.20	39.0
BCF	919.0	32.5	19.2	185.4	178.5	22.3
Floha	848.2	28.6	12.4	6.08	6.96	35.4
Cano Limon	873.4	30.2	19.4	22.6	21.28	30.4

A non-Newtonian fluid is broadly defined as one for which the relationship shear stress/shear rate is not constant. In other words, when the shear rate is varied, the shear stress doesn't vary in the same proportion (or even necessarily in the same direction). The viscosity of such fluids will therefore change as the shear rate varied. These changes are shown in Fig. 10 for the Brent oil and in Fig. 11 for the Floha oil. It has been shown that aerated crude is a non-Newtonian fluid with a more distinct non-Newtonian properties when subjected to intensive aeration (squares in graphs). Results also indicate that non-aerated, fresh crude is almost an Newtonian fluid indicated by almost constant viscosity at varying shear rate (black dots in graphs) and transition into non-Newtonian fluid occurs following the weathering process.

The apparent viscosity of emulsions of different oil/sea water ratios were made and studied in the laboratory conditions. It appeared, that the highest viscosity is observed in the water-in-oil emulsion containing around 35% of oil, as shown in Figures 12 and 13. The emulsion is non-Newtonian fluid. This has been confirmed for Brent and Floha oils emulsified with the sea water in the ratio 2 parts of oil to 8 parts of water. Figures 14 and 15 confirm non-Newtonian behavior of fluid. The most basic graphic method of analyzing non-Newtonian flow is constructing a plot of shear rate versus shear stress. The slope and shape of the resulting curve will indicate the type and degree of flow behavior. If the graph is drawn on log-log paper, the result is frequently a straight line as in Figures 14 and 15.

CONCLUSIONS

Oil spilled in the marine environment undergoes weathering which results in increased viscosity and higher pour and boiling points. The content of oil in water-oil emulsion increases with the age of the spill while the ability of crude to spread due to the viscous and surface tension forces disappeared in oil within a few days of the spill. It has been observed in both open water and in laboratory tests that fractional composition of fresh, light crude changes rapidly to become richer in heavy components.

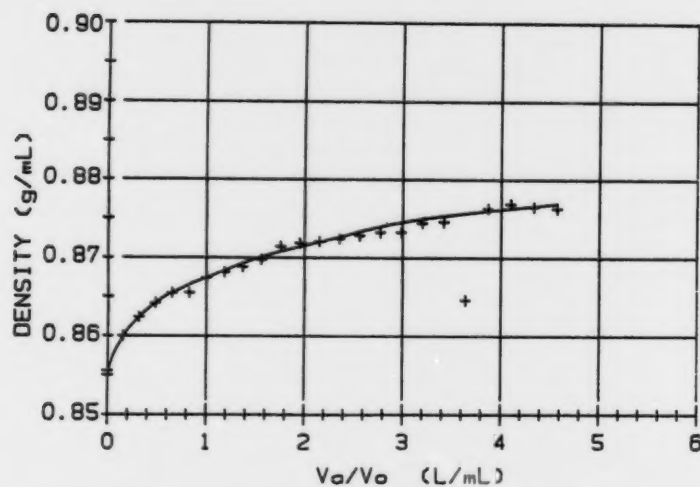


Figure 9. Density change of the Cano Limon crude as a result of the aeration process.

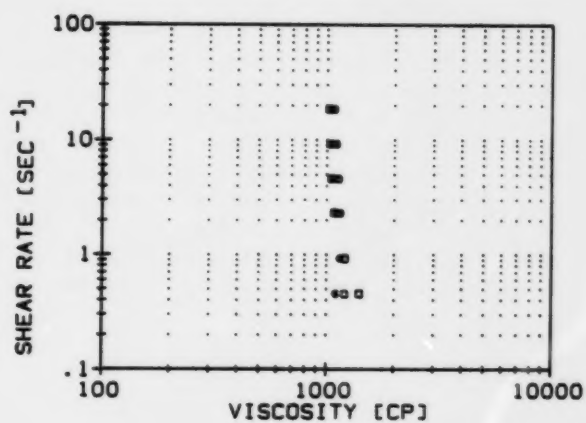


Figure 10. Shear rate vs viscosity for fresh and weathered Brent crude.

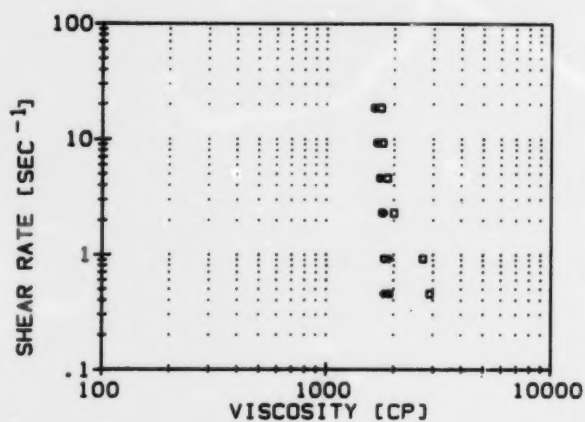


Figure 11. Shear rate vs viscosity for fresh and weathered Floha crude.

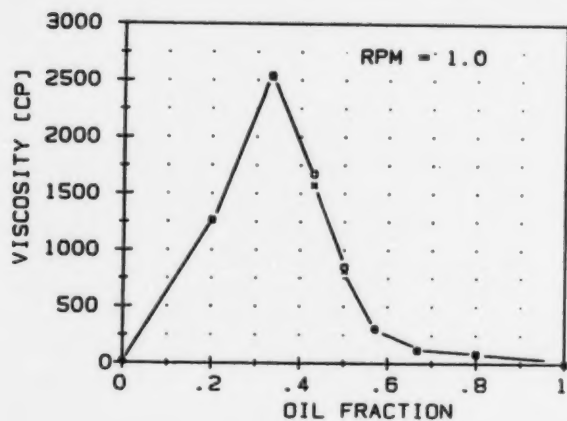


Figure 12. Apparent viscosity of the Brent oil-water emulsions.

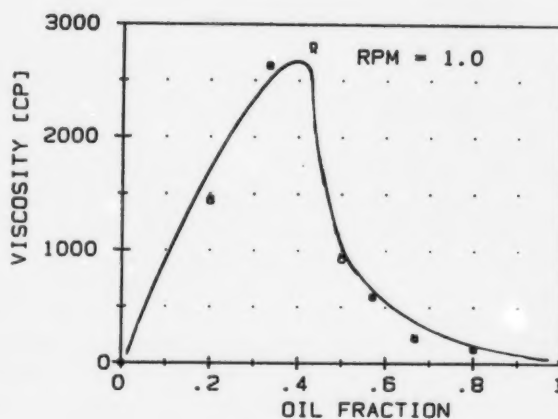


Figure 13. Apparent viscosity of the Floha oil-water emulsions.

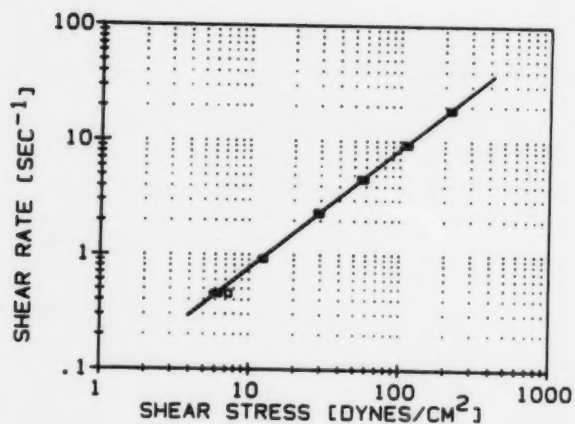


Figure 14. Shear stress vs shear rate for fresh and weathered Brent crude.

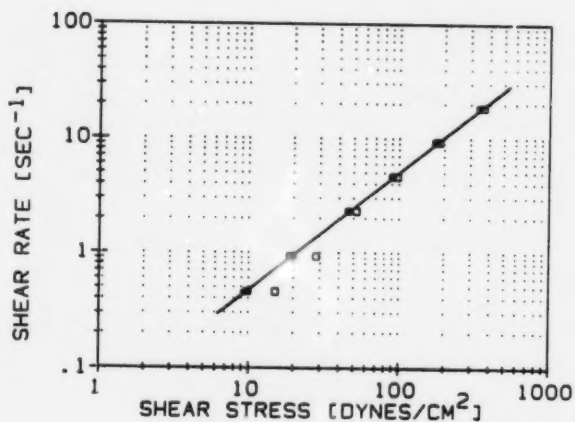


Figure 15. Shear stress vs shear rate for fresh and weathered Floha crude.

Simulation of a natural process of weathering of the oil spill was modeled in the laboratory scale experiments involving gas stripping and formation of oil/sea water emulsions. It was confirmed, that rheology of weathered oil changes, proportionally to the intensity of aeration and emulsification. Products of weathering are non-Newtonian, shear thinning fluids of increased viscosity.

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Photooxidation of Petroleum

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INTRODUCTION

Of all the weathering processes that act upon oil spilled in the environment, photolysis has been one of the least studied. In the environment, the weathering processes occur simultaneously, and differentiating the effects induced by photolysis from changes caused by the other processes can be difficult. Studying the role of photolysis is further complicated by the complex composition of petroleum which means a multitude of photo-induced reactions could conceivably take place, producing an array of photochemical products. Among the photooxidation products that have been identified in previous studies are carbon dioxide, organic acids, carbonyl compounds, hydroxyl compounds, peroxy compounds and sulfoxides. (Freegarde et al. (1971); Hansen (1975); Larson et al. (1978, 1979); Patel et al. (1979); Payne and Phillips (1985); Pengerud et al. (1984); Poston et al. (1988); Sydnese et al. (1985); Tjessem et al. (1983)). Many of these products are more water soluble than their parent compounds and thus, can enhance aquatic toxicity. Photolysis may also lead to polymerization (Daling (1988)). Relatively few studies have examined the changes in physical properties of oil induced by photolysis.

The general purpose of this study was to examine the chemical and physical changes that occur in oils as a result of photooxidation. A variety of crude oils and petroleum products were used to determine how different oils are affected by photolysis, and to examine the importance of photolysis as a weathering process.

The results presented in this paper should be regarded as preliminary information since chemical analysis and identification of photooxidation products using GC/MS techniques has yet to be completed. Final results will be published in the future as an Environment Canada EE-report.

EXPERIMENTAL

Materials

The following oils were used in this study:

Adgo Crude Oil (3.0 % by volume evaporated)
Alberta Sweet Mixed Blend Crude Oil (22.8 % by volume evaporated)
Bent Horn Crude Oil (20.6 % by volume evaporated)
Bunker C Fuel Oil
California (API gravity 15) Crude Oil
California (API gravity 11) Crude Oil
Cold Lake Bitumen
Diesel Fuel Oil
Hibernia Crude Oil (16.0 % by volume evaporated)
Prudhoe Bay Crude Oil (14.6 % by volume evaporated)

Oils that are designated as being evaporated were air stripped at room temperature prior to the experiments. The water used in this study was passed through a Millipore purification unit (reverse osmosis, activated carbon and ion-exchange). Bio-crystal marine-mix was added to the water to produce a synthetic sea water of 33 ‰ salinity and 0.02% by weight mercuric chloride was added as an antiseptic. The water was filtered through a 0.2 μ m Millipore filter prior to use.

Photolysis

Exposure vessels consisted of 190 mm diameter X 100 mm high, Pyrex crystallizing dishes filled with 2100 mL of water. 26.9 mL of oil was layered upon the water resulting in an initial oil film with an average thickness of 1 mm. The vessel was covered with a 6 mm thick quartz plate which was positioned 8 mm above the rim of the crystallizing dish. The gap between the rim of the dish and the quartz plate was left open to allow normal air flow over the oil surface. A narrow stainless steel tube was inserted into the water layer and held in position so that water could be added to the system without disturbing the oil film if evaporation caused a decrease in the water level. For each oil sample that was exposed to photolysis, a duplicate sample was simultaneously subjected to the same conditions except in a vessel that was completely opaque to light. These samples which were shielded from irradiation were termed "dark controls". The water layer was stirred daily for 90 seconds by a 25 mm egg-shaped stirring bar at 60 RPM. This mixing speed was not of sufficient energy to cause deformation of the oil/water interface for the fresh oils. Some deformation of the interface and shearing of droplets was noticed during mixing of some samples after irradiation.

Photolyses in sunlight were carried out in an unobstructed location free of any reflections or shadows on a roof in Ottawa, Ontario (latitude: 45° 24'N). Experiments were performed during the months of August to mid-October. Sunlight intensity during exposure was measured using p-nitroacetophenone / pyridine actinometry (Dunlin and Mill (1982)).

Experiments were also conducted under fluorescent UVA-340 40-watt lamps (Q-Panel Company) at 22 +/- 2°C. The manufacturer claims that the lamp's emission is an excellent simulation of sunlight from 370 nm down to the solar cut-off of 295 nm. Results from this phase of the study are not reported in this paper.

Analysis

At the termination of each experiment, surface oil was separated from the water phase. The mass of oil remaining on the surface was determined gravimetrically. The water phase was filtered through a 1.0 μ m Millipore filter and the mass of "sedimented" oil on the filter was determined. Physical properties were determined for the surface oil samples by the analytical methods listed below:

- | | |
|------------------------|------------------------------|
| - density | ASTM method D4052-81 |
| - viscosity (dynamic) | Brookfield Viscometer |
| - interfacial tensions | ASTM method D971-82 |
| - asphaltene content | hexane insoluble precipitate |

All measurements were determined at 15°C.

The natural dispersibility and chemical dispersibility of selected oils were determined using the Swirling Flask Apparatus described by Fingas (1988) and Enersperse 700 dispersant at an oil-to-dispersant ratio of 25:1.

The oil content of the water phase, after filtering, was monitored using a Horiba OCMA-220 Oil Content Analyzer. The Horiba Analyzer was calibrated using a standard mixture of iso-octane, cetane and benzene. The total carbon content of the water phase was measured using a Xertex-Dohrmann DC-80 Series Carbon Analyzer. The pH of water was also determined.

Water samples were extracted using multiple batch extractions of ethyl acetate as described by Aaberg et al. (1985), and the extracts were then concentrated under vacuum. Concentrated extracts and surface oil samples were fractionated by gel chromatography using lipophilic Sephadex LH-20 dextran gel and mixtures of chloroform, methanol and ethanol as described Barth et al. (1981). This fractionation technique separates compounds according to degree of polarity. Preliminary GC/FID results indicate good separation of compounds. Further characterization and identification of photooxidation products are to be

performed using GC/MS and will be published in the future.

Selected water and oil samples were examined at various times during the experiment for the presence of microbial activity. No micro-organisms were detected when the samples were subjected to microscopic examination or when inoculated nutrient mediums were incubated.

RESULTS AND DISCUSSION

Table 1 summarizes some of the physical manifestations that were attributed to photolysis. Water beneath irradiated oils acquired a yellowish hue. The intensity of this hue varied from oil to oil, and increased with exposure time. Water beneath shielded oils exhibited no colour change. As noted in the table, precipitates formed in some of the oils during irradiation and some oils developed a crust-like formation at the air-oil interface. Neither of these phenomena were observed in the shielded oils.

Figures 1 to 4 show the change in density as a function of time for exposed oil samples and for shielded oil samples. All samples display an increase in density with time. Increases in density of the shielded (dark) samples can be attributed to the loss of volatile components due largely to evaporation and to a lesser degree, to dissolution. Except for two of the oils, California 15 crude oil and Diesel fuel, the irradiated samples had greater densities than those which were shielded. Possible explanations of why photolysed oils exhibit greater densities than unphotolyzed oils are probably a combination of effects caused by solar irradiation that include: i. the formation of photooxidation products that are denser than their hydrocarbon parents; ii. the formation of photooxidation products that are easily depleted from the surface oil by evaporation and dissolution; and iii. photolysis enhances evaporation by causing an increase in surface temperature of the the oil. The temperatures of oil and water phases were monitored for some oils during the experiment and the maximum recorded difference between exposed and dark samples was 3°C. Possible explanations of why the exposed California 15 crude oil and the exposed Diesel fuel oil were less dense than the unexposed samples are: i. photolysis causes a build up of compounds at the air/oil interface which forms a resistive barrier to evaporation and thereby, reduces volatilization of compounds from the underlying oil; and ii. photo-induced reactions remove dense oil phase compounds. The physical changes noted in several of the oils during irradiation (see Table 1) would provide some support for first theory. Hard crustal material did form on the surface of the California 15 crude oil and the oil beneath this crust was relatively fresh in appearance. No crust formation was observed in the Diesel fuel, but

precipitous matter was observed. This precipitous material collected at the oil-water interface and eventually entered the water phase. It could be postulated that this photo-induced precipitation resulted in the removal of the more dense constituents from the oil.

The density measurements also show that several of the oils attained densities that approached or exceeded that of water. California 15, California 11 and Adgo crude oils, and Cold Lake bitumen, all achieved a density of 1 g/mL or greater during the experiments. If these oils were spilled in a marine environment, it is likely that these oils would submerge. As Figures 2, 3 and 4 demonstrate, exposure to solar radiation accelerates an increase in density in some of these oils. The density results obtained in this experiment for California 15 and California 11 crude oils, Bunker C and Cold Lake bitumen are similar to those obtained by Lee et al. (1989).

The measured viscosities of the oil samples are presented in Table 2. For exposure times of 10 days or less, the irradiated oils had significantly higher viscosities than the shielded samples. For exposure times of 20 days or more, the irradiated oils had viscosities that were approximately equal to or slightly less than those of the shielded samples. Photo-polymerization could result in higher viscosity (Daling and Branvik (1988)). The results indicate that effects of photolysis on viscosity over a short term (approximately 10 days or less) can be significant but over a longer term, the effects of photolysis on viscosity will be insignificant compared to the effects of evaporation.

Table 3 presents the measured oil-seawater interfacial tensions. For each oil, the photolysed sample had a lower interfacial tension relative to the shielded oil. Dramatic reductions in interfacial tensions for the irradiated samples of Diesel, Bent Horn crude oil and Adgo crude oil indicate that photooxidation results in the formation of surface-active products. Daling (1988) demonstrated that these photo-produced surfactants play an important role in the emulsification process.

The asphaltene content of surface oil samples are shown in Table 4. Photolysed samples generally had higher asphaltene contents than shielded samples. This increase in asphaltene content could be due to the formation of macro-molecules by photo-polymerization and/or to a concentration effect caused by the removal of photooxidized components from oil. All oils, both exposed and shielded samples, exhibit a general increase in asphalenes as a function of time, except for Diesel and Bent Horn crude oil. The asphaltene content of Diesel and Bent Horn crude reached a maximum value after 3 days of exposure and then steadily declined with time. This trend is seen in both the exposed and shielded samples.

The natural dispersibilities of the oil samples listed in Table 5 were measured; all of the samples essentially had no natural dispersibility as measured by the Swirling Flask apparatus. Therefore, the photo-produced surfactants present in these oils have no noticeable affect upon natural dispersibility. The chemical dispersibilities of these samples are summarized in Table 5. The effect of photooxidation on chemical dispersibility was extremely dependent upon the oil. The effectiveness of Enersperse 700 on photolysed Diesel, ASMB crude oil and Prudhoe Bay crude oil was approximately half of the value obtained with non-photolysed samples. Photolysis had no significant influence upon the chemical dispersibility of Adgo and Bent Horn crude oils.

Table 1: Observations

Oil	Physical Changes During Irradiation
Diesel	- within an hour of irradiation the oil's colour began to change from a brownish yellow to a pale yellow and a precipitate formed at the oil/water interface - within six hours the water had a yellowish colour and became turbid - the colour of both the water and oil phases became more intensely yellow with irradiation
Bent Horn Crude	- within two hours an orange precipitate was forming in the oil layer - within two days the water had a yellowish colour and became turbid - the oil became more intensely orange and the water more yellow with irradiation
Adgo Crude	- within six hours the oil's colour began to change from a medium brown to a brownish orange - within three days the water had a yellowish colour
California 15 Crude	- within three days a "skin" had formed at the air/oil interface - within six days the skin becomes slightly encrusted - amount crustal material present increases with time - crustal material flakes off and sinks - after twenty-one days parts of the oil film are overwashed with water and in these areas some bleaching is present - oil beneath crust appears to be relatively fresh - water phase is only slightly coloured
California 11 Crude	- same observations as for California 11 Crude but less crustal material is formed
Cold Lake Bitumen	- small amount of crust formed - water phase is only slightly coloured
ASMB Crude	- small amount of greyish crust formed - water phase is only slightly coloured
Prudhoe Bay Crude	- little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Hibernia Crude	- little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Bunker C	- small amount of crust formed - water phase is only slightly coloured

TABLE 2: VISCOSITY (CP)

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	3.00	5.80	9.80	-	-	-
DIESEL	EXPOSED	3.00	7.60	16.80	-	-	-
BENT HORN	DARK	1500	8900	73200	-	108400	-
BENT HORN	EXPOSED	1500	38700	76400	-	78500	-
CALIFORNIA	DARK	6400	1400000	>1500000	-	>1500000	-
15 CRUDE	EXPOSED	6400	>1500000	>1500000	-	>1500000	-
CALIFORNIA	DARK	34000	1100000	>1500000	-	>1500000	-
11 CRUDE	EXPOSED	34000	1150000	>1500000	-	>1500000	-
COLD LAKE	DARK	235000	520000	>1500000	-	>1500000	-
BITUMEN	EXPOSED	235000	600000	>1500000	-	>1500000	-
ASHB	DARK	135	1800	2750	-	368000	-
CRUDE	EXPOSED	135	2080	3020	-	387000	-
ADGO	DARK	75	-	-	23900	-	-
CRUDE	EXPOSED	75	-	-	50200	-	-
BUNKER C	DARK	48000	-	-	480000	-	1300000
PRUDHOE	EXPOSED	48000	-	-	500000	-	1500000
BAY CRUDE	DARK	182.5	-	-	1050	-	16500
BAY CRUDE	EXPOSED	182.5	-	-	2080	-	20000
HIBERNIA	DARK	50000	-	-	87000	-	144200
CRUDE	EXPOSED	50000	-	-	127000	-	113200

TABLE 4: ASPHALTENE CONTENT (WEIGHT %)

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	2.43	4.42	2.50	-	1.49	-
DIESEL	EXPOSED	2.43	4.28	2.07	-	1.38	-
BENT HORN	DARK	3.63	4.22	2.64	-	1.56	-
CRUDE	EXPOSED	3.63	6.27	3.65	-	1.00	-
CALIFORNIA	DARK	18.89	24.21	22.60	-	19.50	-
15 CRUDE	EXPOSED	18.89	22.87	22.85	-	21.73	-
CALIFORNIA	DARK	17.61	19.56	20.86	-	21.98	-
11 CRUDE	EXPOSED	17.61	20.87	21.54	-	23.01	-
COLD LAKE	DARK	12.29	13.71	14.81	-	13.59	-
BITUMEN	EXPOSED	12.29	14.94	17.08	-	16.50	-
ASHB	DARK	3.55	4.85	4.46	-	4.38	-
CRUDE	EXPOSED	3.55	6.08	6.15	-	8.21	-
ADGO	DARK	2.63	-	-	2.19	-	7.25
CRUDE	EXPOSED	2.63	-	-	2.25	-	7.28
BUNKER C	DARK	6.33	-	-	6.59	-	6.86
PRUDHOE	EXPOSED	6.33	-	-	7.45	-	8.53
BAY CRUDE	DARK	4.66	-	-	5.72	-	6.02
BAY CRUDE	EXPOSED	4.66	-	-	6.87	-	9.36
HIBERNIA	DARK	3.43	-	-	3.82	-	3.79
CRUDE	EXPOSED	3.43	-	-	4.51	-	6.25

TABLE 3: OIL - WATER INTERFACIAL TENSION (mN/m)

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	20.30	24.50	24.70	-	I / S	-
DIESEL	EXPOSED	20.30	5.10	2.00	-	I / S	-
BENT HORN	DARK	13.80	11.80	9.70	-	I / S	-
CRUDE	EXPOSED	13.80	10.40	2.70	-	I / S	-
ASHB	DARK	22.50	26.00	26.50	-	I / S	-
CRUDE	EXPOSED	22.50	25.40	25.00	-	I / S	-
ADGO	DARK	23.10	-	-	16.50	-	22.40
CRUDE	EXPOSED	23.10	-	-	9.60	-	12.70
PRUDHOE	DARK	26.80	-	-	28.20	-	30.90
BAY CRUDE	EXPOSED	26.80	-	-	25.70	-	27.20
HIBERNIA	DARK	16.90	-	-	44.50	-	46.50
CRUDE	EXPOSED	16.90	-	-	43.70	-	44.70

NOTE: I / S = INSUFFICIENT SAMPLE

TABLE 5: CHEMICAL DISPERSIBILITY (WEIGHT % DISPENSED)

OIL	CONDITION	TIME (DAYS)		DARK SAMPLE	EXPOSED SAMPLE
		3	79		
DIESEL	DARK	3	79	43	-
BENT HORN	DARK	3	16	19	-
CRUDE	EXPOSED	6	13	16	-
ASHB	DARK	3	19	7	-
CRUDE	EXPOSED	6	13	7	-
ADGO	DARK	10	22	19	-
CRUDE	EXPOSED	25	2	2	-
PRUDHOE	DARK	10	8	4	-

Figure 1: Density versus time

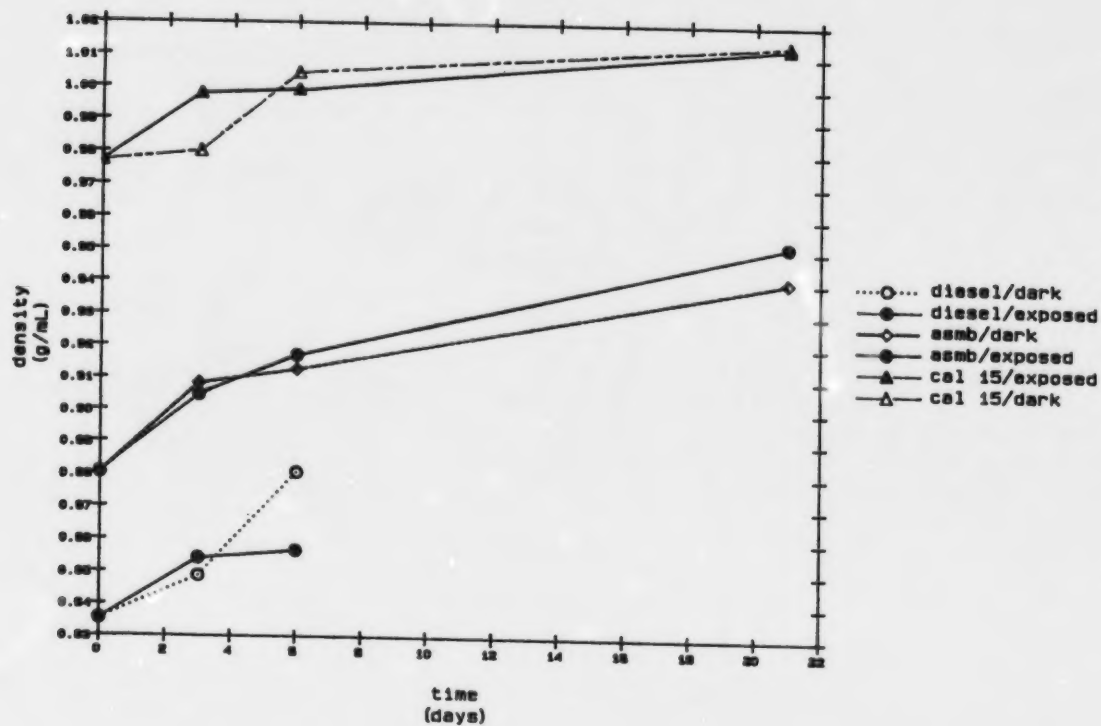


Figure 2: Density versus time

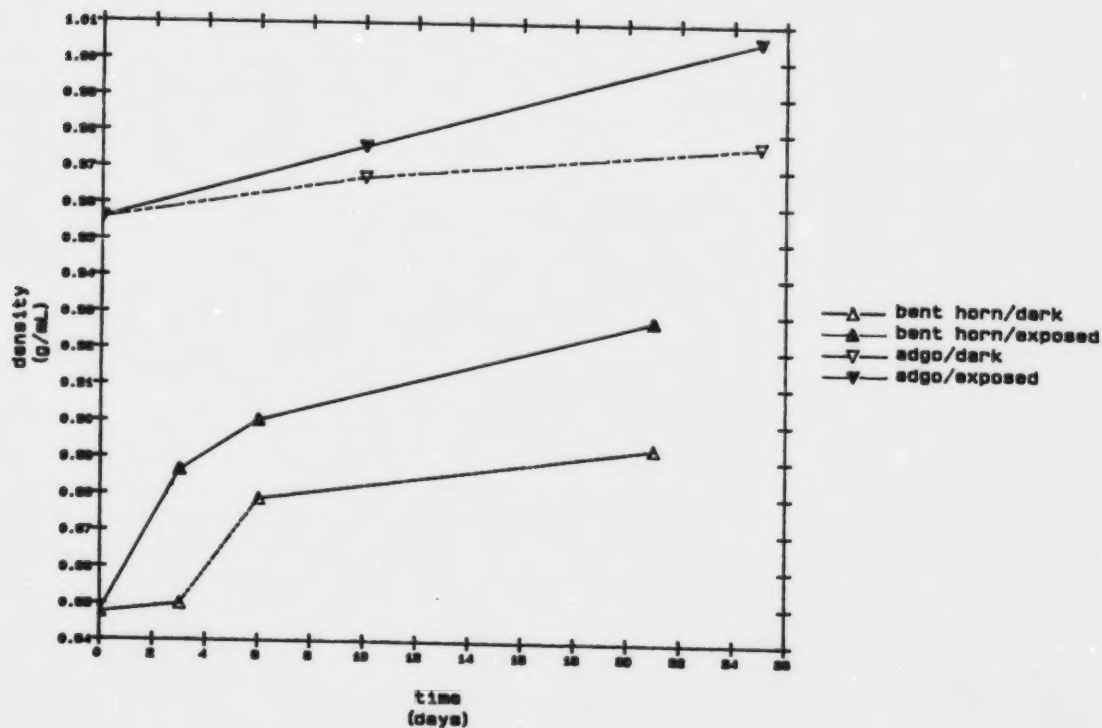


Figure 3: Density versus time

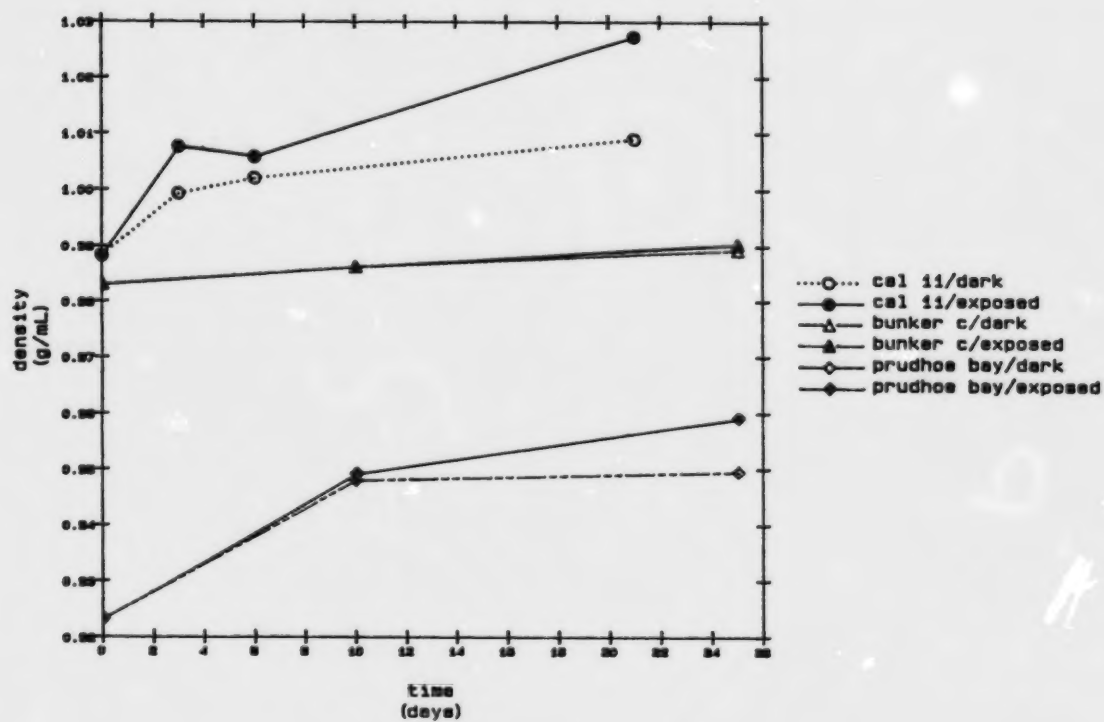
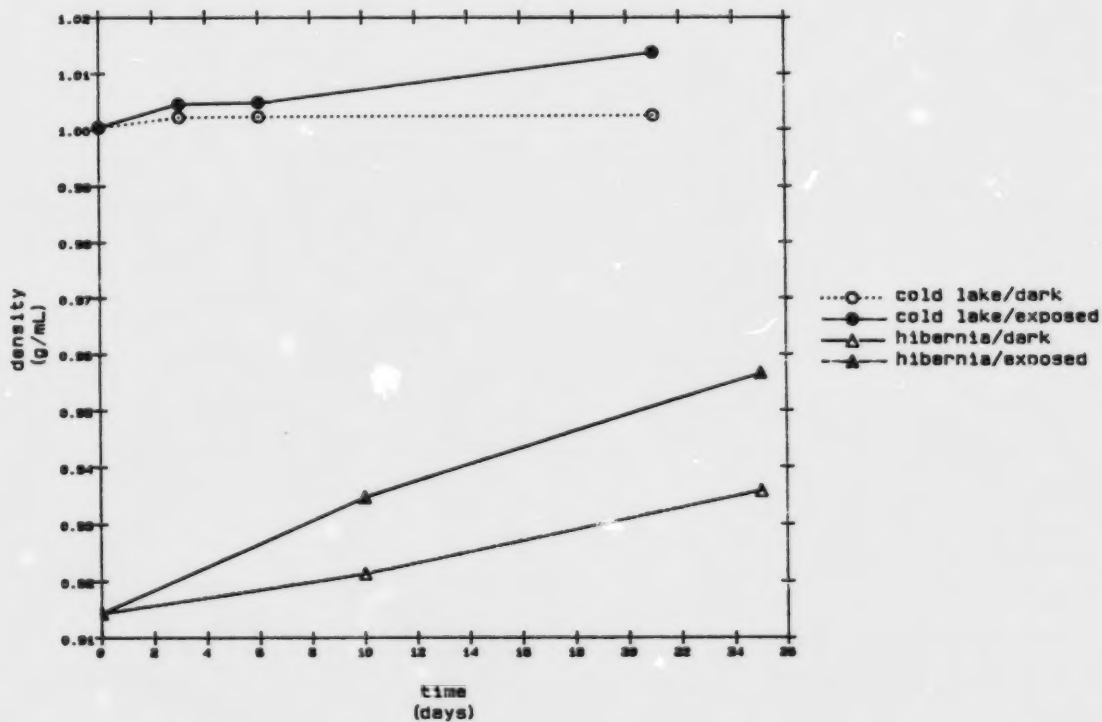


Figure 4: Density versus time



Figures 5 to 8 show the amount of oil in water measured by the Horiba Analyzer as a function of time. Similarly, the measured carbon content of water are presented in Figures 9 to 12. Since the water was filtered prior to performing these measurements, only dissolved molecules and sub-micron particles would be present in the water. In each case, the amount of material measured in the water was higher for irradiated samples. As noted in the observations (Table 1), water beneath irradiated oil became yellowish during exposure. The visual intensity of the yellow colour appeared to directly correlate with the measured carbon content. Previous studies have shown that photooxidation products from fuel oils are highly water soluble. (Poston et al. (1988); Herbes and Whitley (1983)) The higher oil content in the water under irradiated oil films suggests that the presence of photooxidized compounds leads to an increase in the amount of oil incorporated into water. The photooxidation products could possibly act as co-solvents which enhance the solubility of hydrocarbons in water. The photooxidation products probably also act as surfactants that stabilize sub-micron oil-in-water emulsions. GC/FID fingerprint tracings indicated that the hydrocarbon composition of water extracts were very similar to those of the surface oils; this would suggest that much of the oil measured in the water is in the form of oil-in-water emulsions.

Changes in the pH of water as a function of exposure time are presented in Figures 13 and 14. The pH of water beneath shielded oils exhibited no change with time and remained constant at a value of 8.5 ± 0.2 . The water beneath Diesel fuel oil and Bent Horn crude oil showed a sharp decrease in pH during irradiation. After 21 days, these water layers had pH readings of about 4. This clearly indicates that the photooxidation products formed by these oils are acidic in nature. The formation of organic acids during fuel oil irradiation had also been noted by Larson et al. (1979). Several studies have compared the toxicity of non-photolysed oil to photolysed oil, and they have shown that photolysis enhances toxicity. Our results indicate that if the species used in bioassays are sensitive to pH, the simple change in pH might be a factor. Under real marine spill conditions, it is unlikely that changes in pH would occur because of the buffer effect from surrounding water.

Although the results show that photolysis can significantly influence the amount of oil that enters the water column through dissolution and emulsification, a mass balance shows this quantity to be far less than 1% of the total mass of oil spilled. Figures 15 to 24 show a mass balance for each oil. Each graph illustrates what percent of the original mass of oil remained on the surface as a film (labelled 'SUR' on the graph); what percent of the oil evaporated ('AIR'); and what percent of the oil sank ('SED'). The quantity of oil that evaporated was calculated from the amounts measured in the other phases. At time zero (0 days), 100 % of the oil was on the surface. It should be again be mentioned that some of the oils were artificially evaporated prior to being used. This amount of pre-test evaporation is not included in these calculations. From these graphs, it is apparent that the importance of photolysis to the fate of an oil is dependent upon the oil itself. Exposure to solar radiation resulted in an increase in the amount of oil that "sedimented". Shielded oils had little sediment ($< 0.1\%$). Significant amounts of sedimented oil formed when California 11 and California 15 crude oils were irradiated; after 21 days of exposure, the percentage of oil that sedimented was 7 and 9 %, respectively.

Figure 5: Oil-in-water content versus time
Horiba Analyzer results

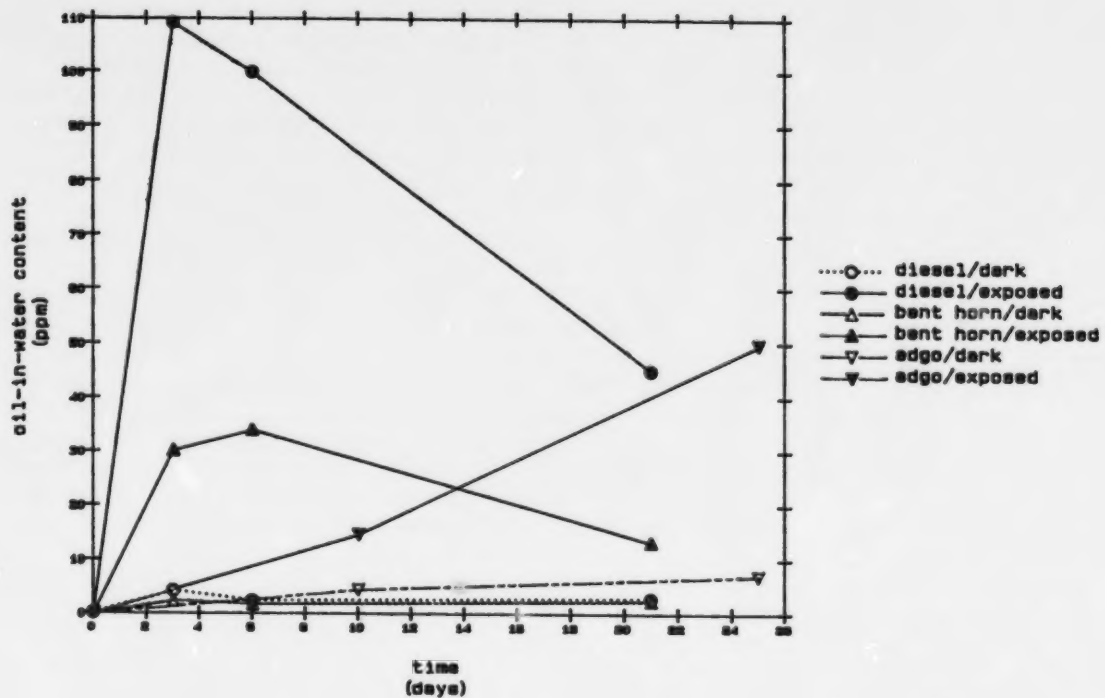


Figure 6: Oil-in-water content versus time
Horiba Analyzer results

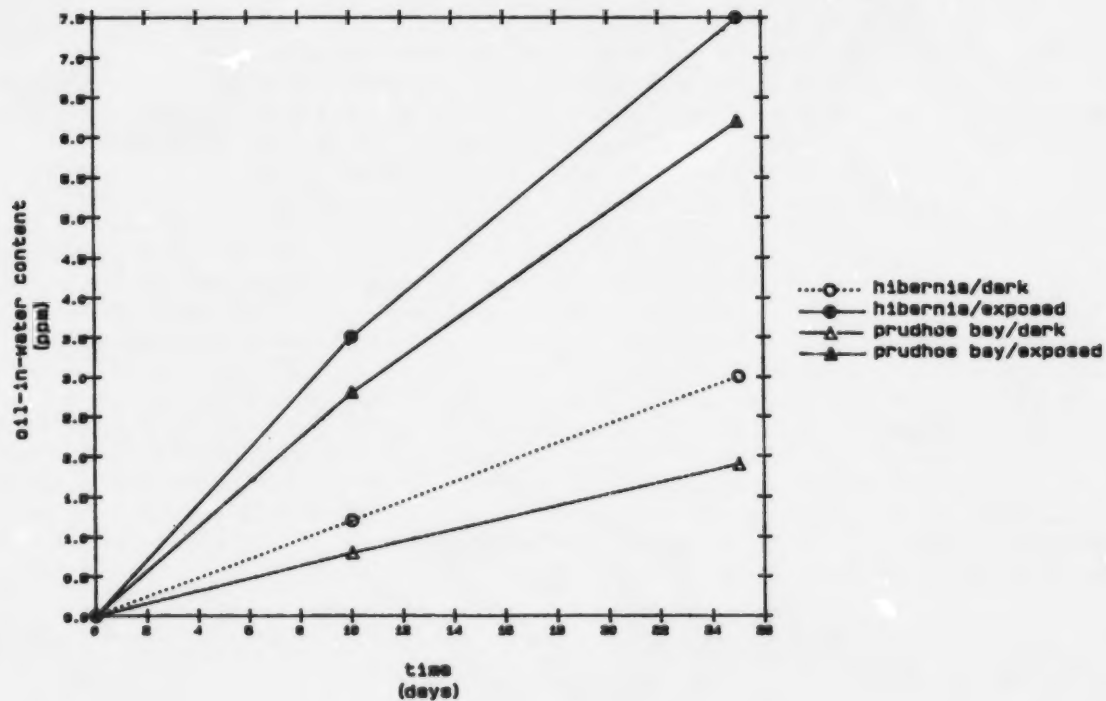


Figure 7: Oil-in-water content versus time
Horiba Analyzer results

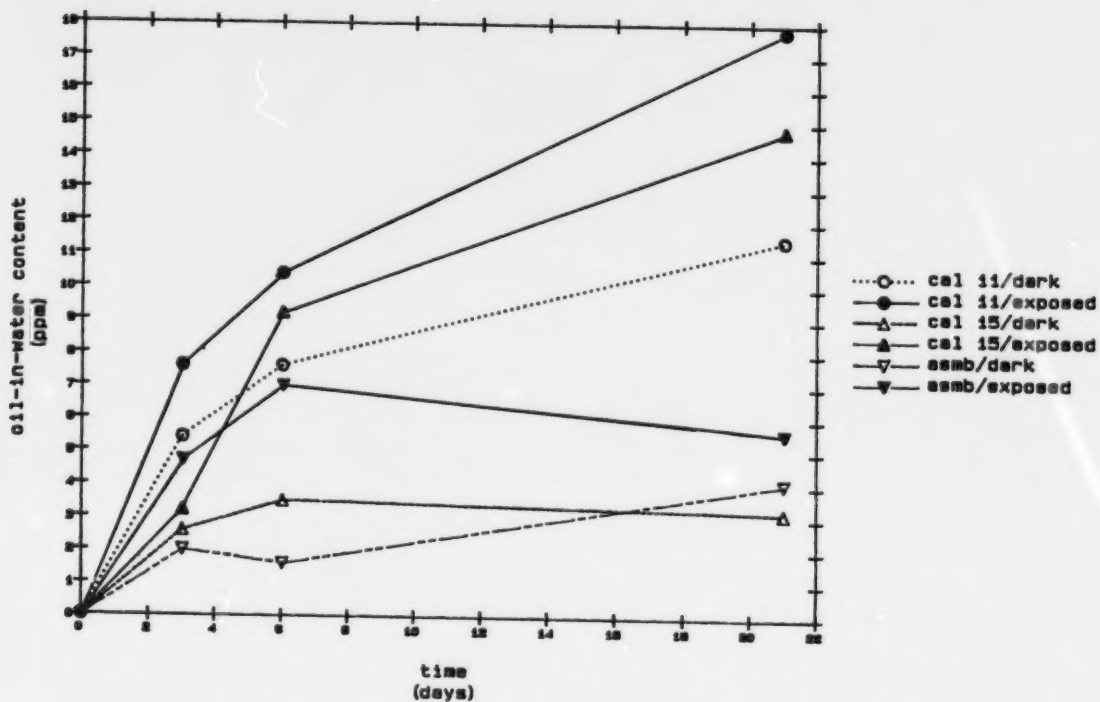


Figure 8: Oil-in-water content versus time
Horiba Analyzer results

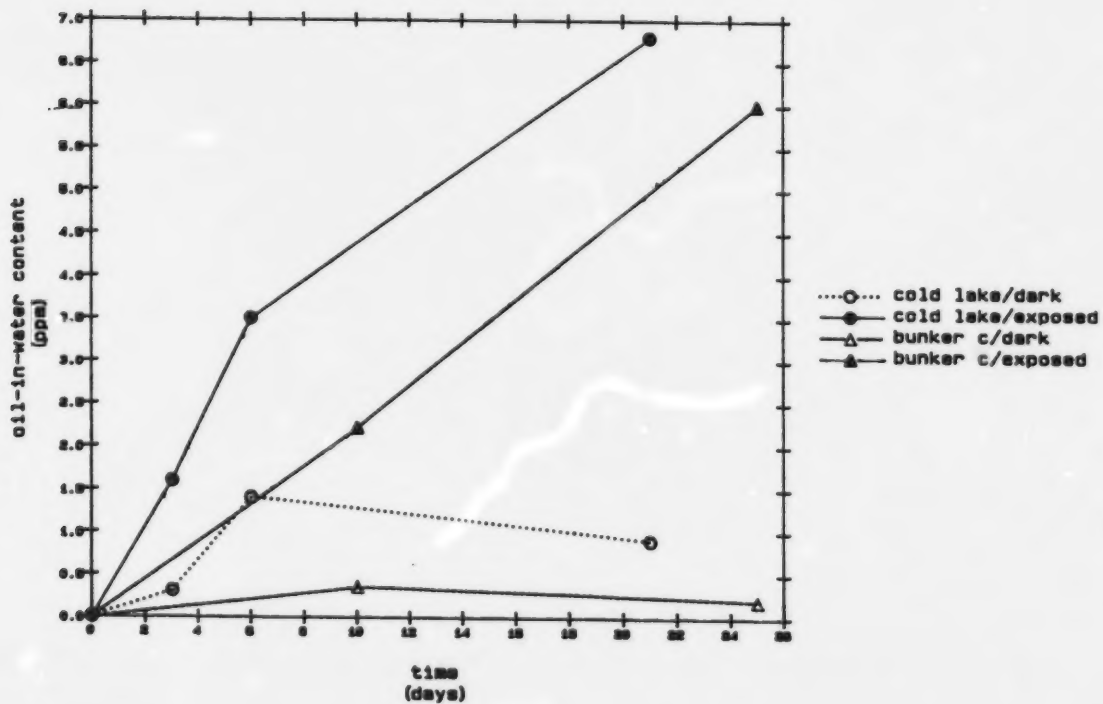


Figure 9: Carbon Content of Aqueous Phase

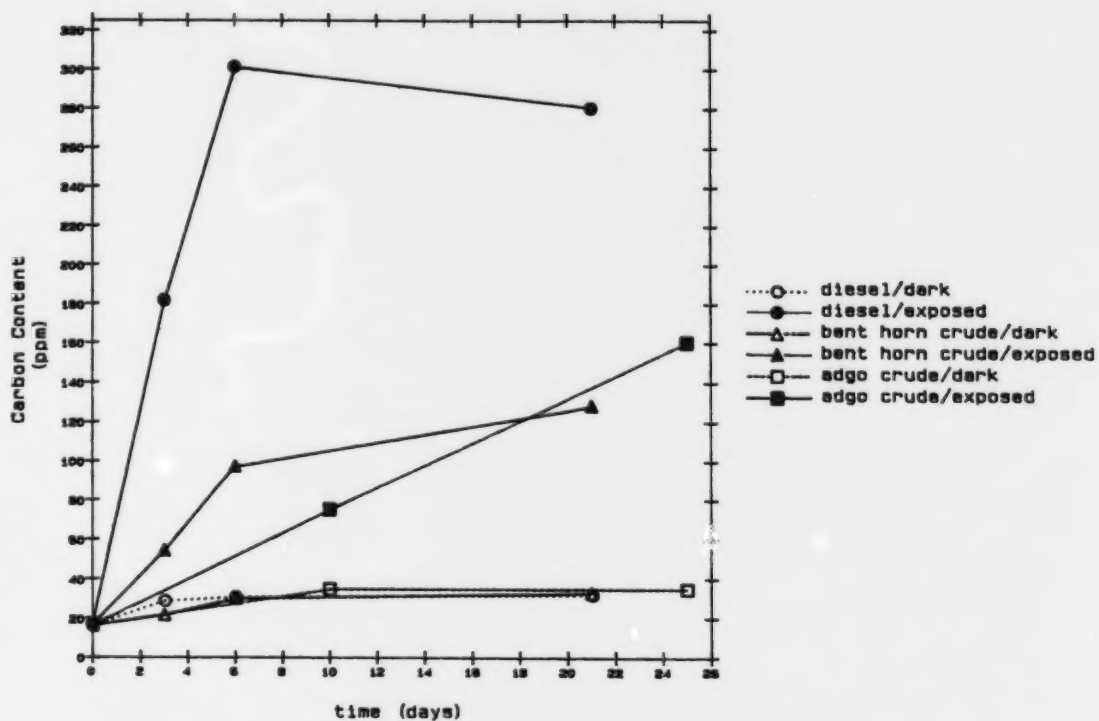


Figure 10: Carbon Content of Aqueous Phase

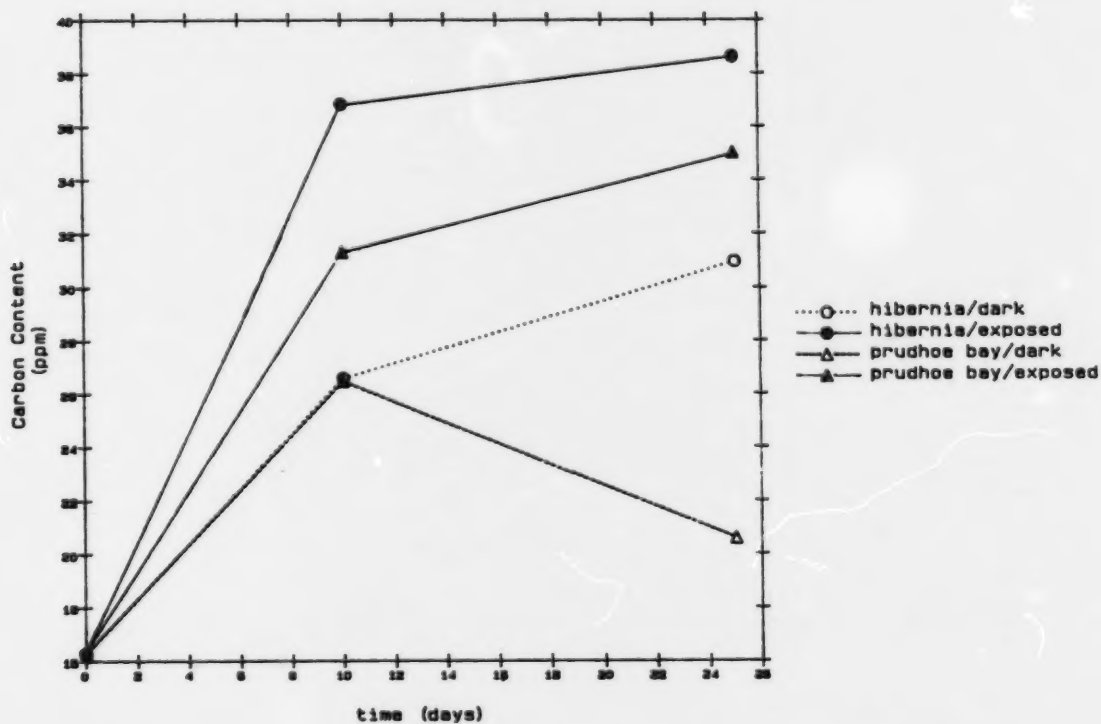


Figure 11: Carbon Content of Aqueous Phase

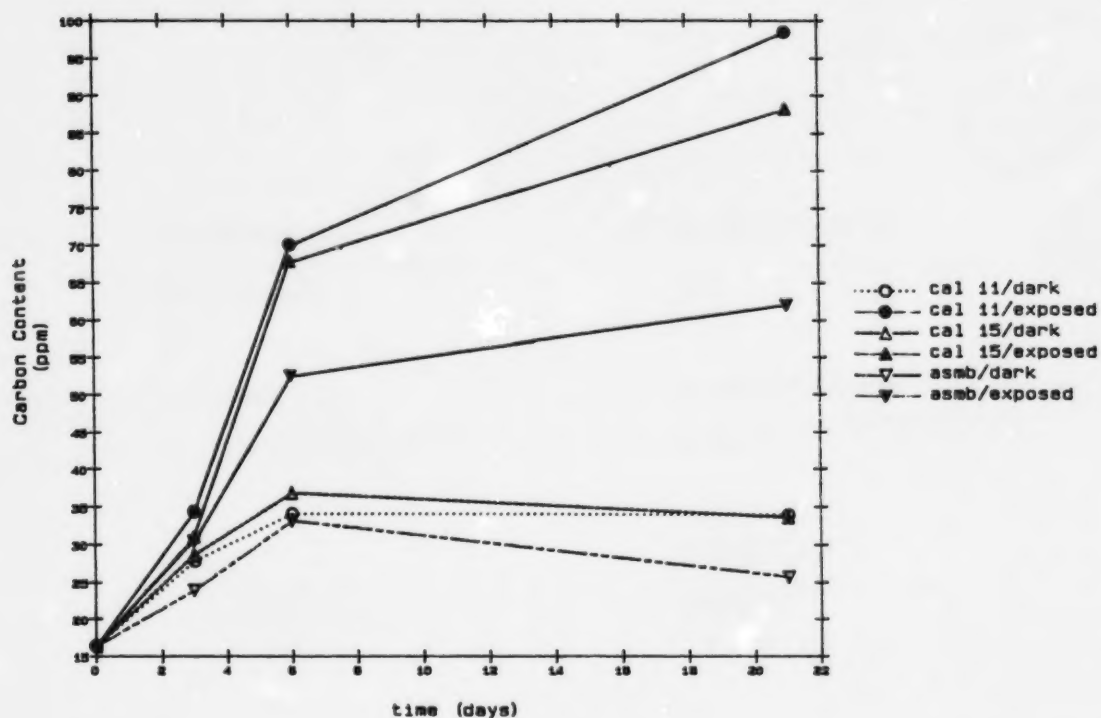
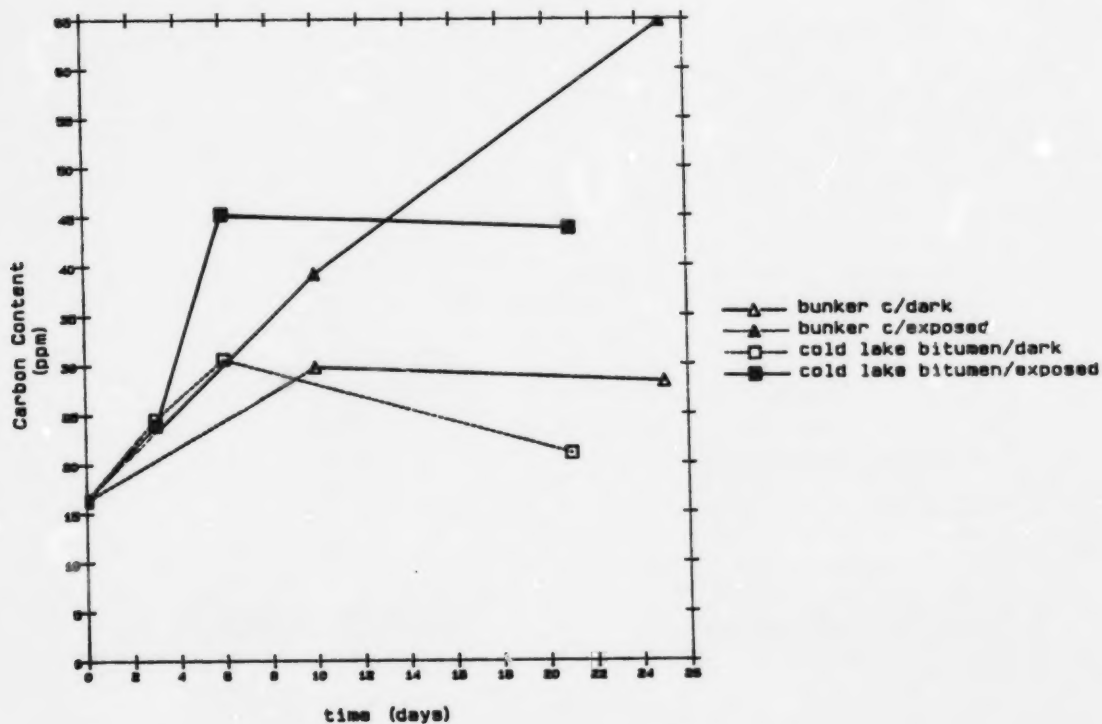


Figure 12: Carbon Content of Aqueous Phase



Mass Balances For Oils

Figure 13: pH of Aqueous Layer

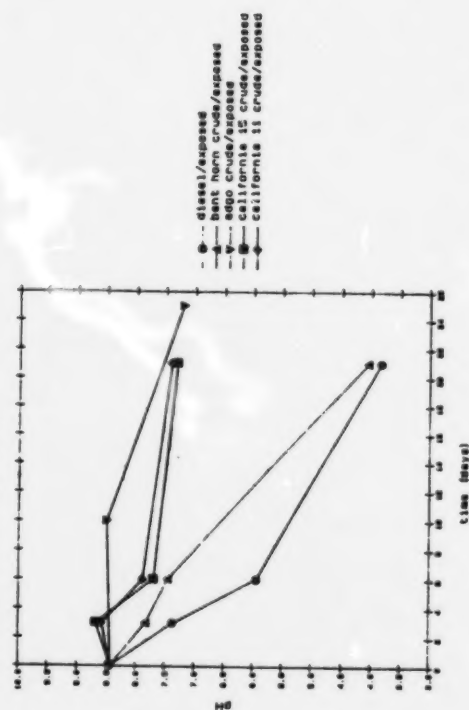


Figure 14: pH of Aqueous Layer

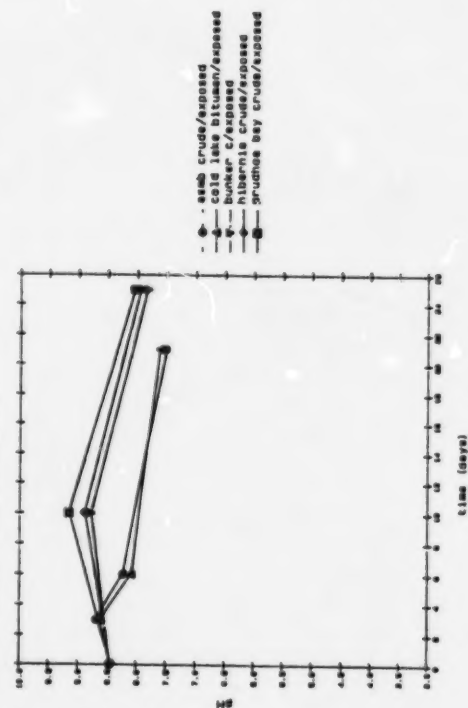
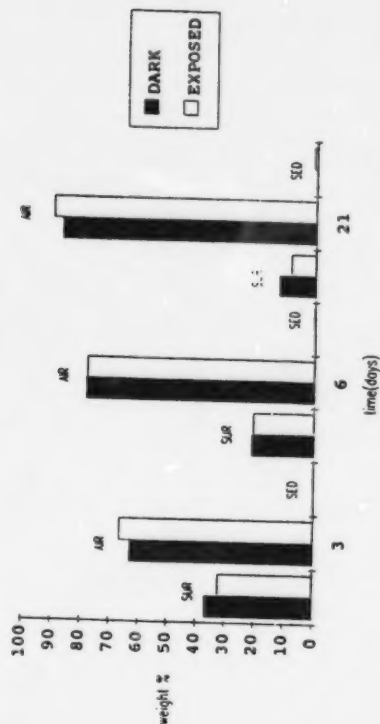


Figure 15:

diesel fuel oil



AIR = Air
SED = Sediment
SUR = Surface

Figure 16:

bent horn crude

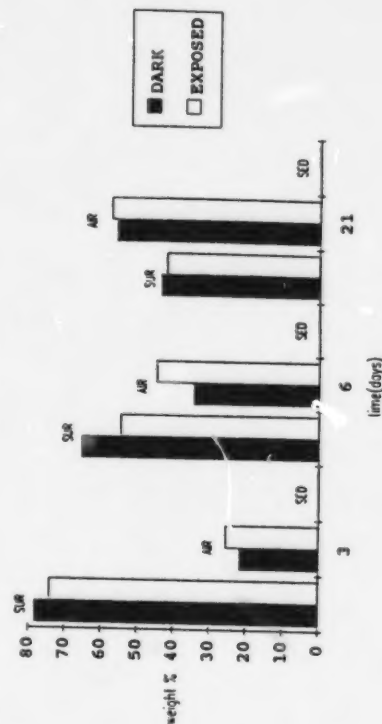


Figure 19: california 11 crude

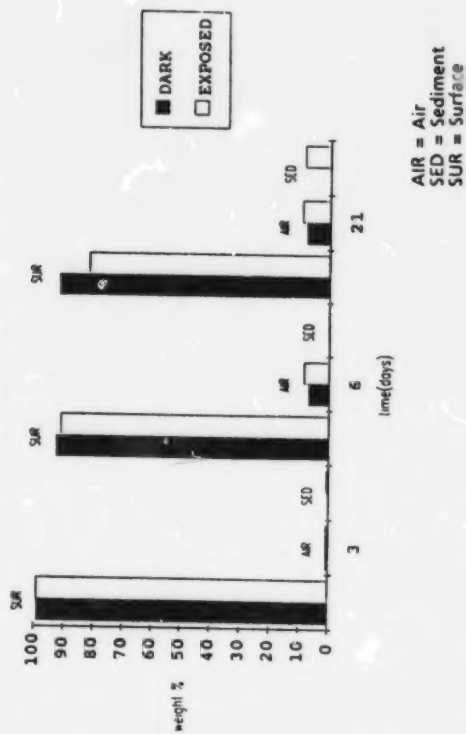


Figure 20: cold lake bitumen

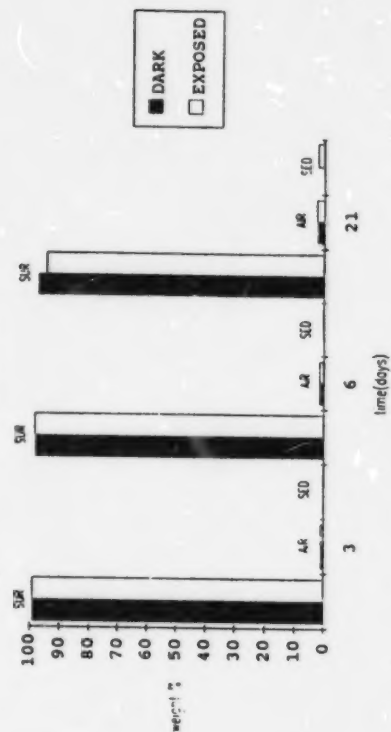


Figure 17: adgo crude

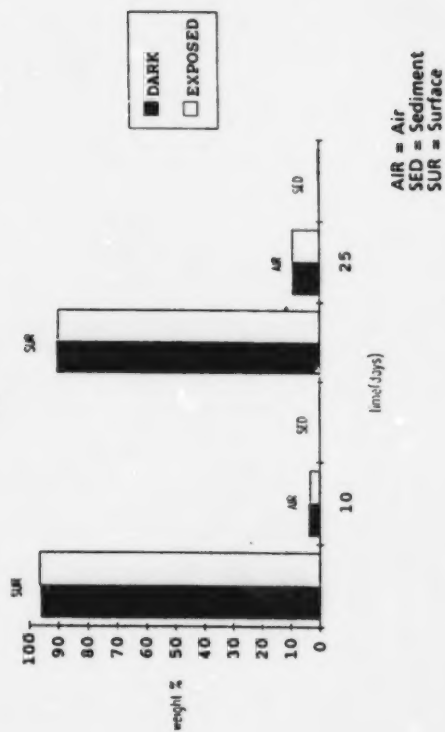


Figure 18: california 15 crude

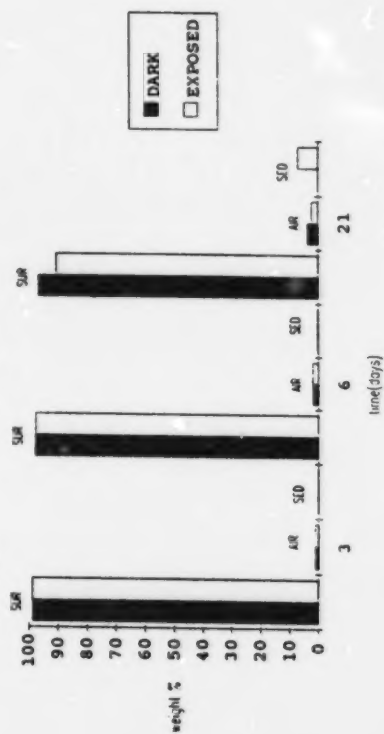
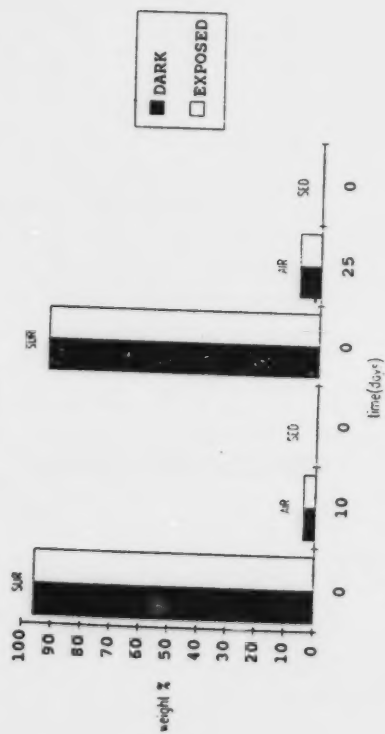


Figure 21: hibernia crude



AIR = Air
 SED = Sediment
 SUR = Surface

Figure 22: bunker c fuel oil

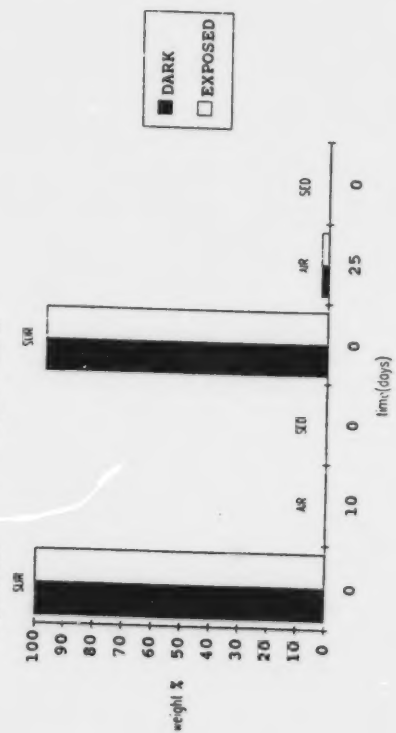
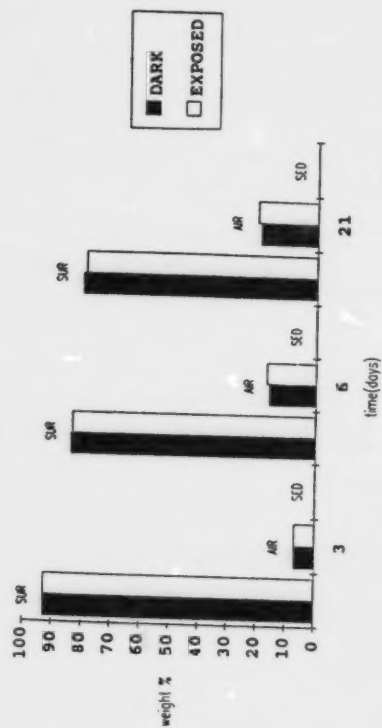
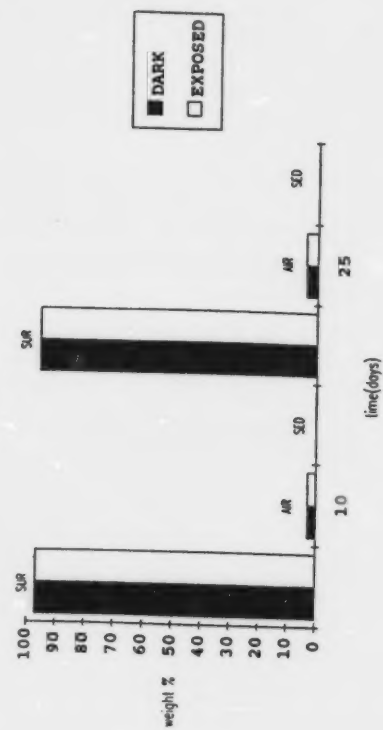


Figure 23: alberta sweet mixed blend crude



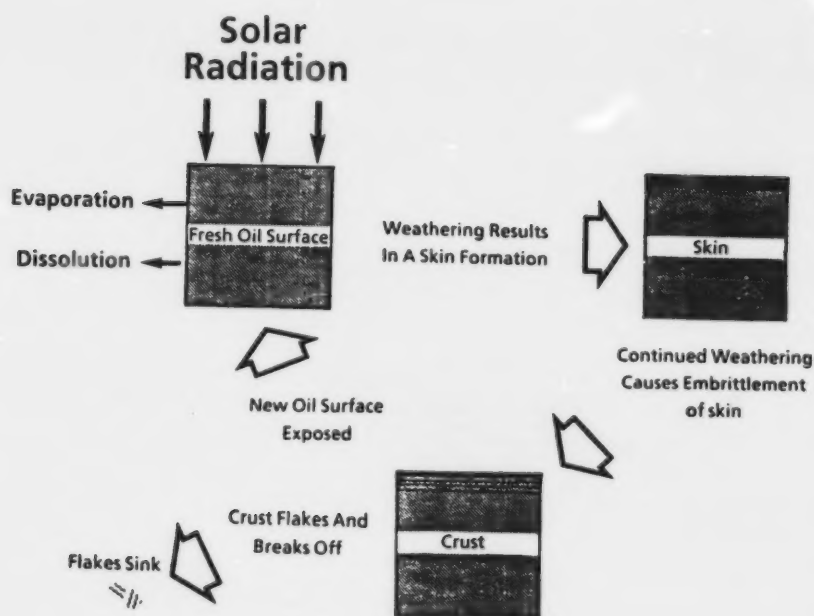
AIR = Air
 SED = Sediment
 SUR = Surface

Figure 24: prudhoe bay crude



From the physical changes observed in oils (Table 1) and from the results obtained, it is concluded that photo-induced reactions are responsible for the formation of materials which encrust oil. Figure 25 is a simple schematic diagram that illustrates how oil "crust" is formed. As oil weathers, a "skin" of dense material forms at the air-oil interface. This skin was observed to form on oils that were photolysed as well as on oils that were shielded. If this material is subjected to photolysis, it becomes embrittled thus forming a hardened crustal material. No crust was formed on oils kept in the dark. Further exposure causes the crustal material to form flakes which eventually break off and sink, thus exposing a new oil surface. The crusts observed in this study are similar in description to those found on tar balls by Morris et al. (1977).

Figure 25: CRUST FORMATION



CONCLUSIONS

The importance of photolysis as a weathering process will depend very much upon the type and composition of the oil. This study has identified several oils which are extremely sensitive to photooxidation, and it has demonstrated how photo-induced reactions can influence the fate and behaviour of these oils. Photolysis induced changes in physical properties and resulted in the formation of products that increased the amount of oil entering the water column.

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TAINTING IN SEA SCALLOPS (Placopecten magellanicus) EXPOSED TO THE
WATER-SOLUBLE FRACTION OF CRUDE OIL AND NATURAL GAS CONDENSATE

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ABSTRACT

Tainting was examined in sea scallops (Placopecten magellanicus) exposed to the water-soluble fraction (WSF) of Ninian crude oil and Scotian Shelf natural gas condensate for periods of 3 h to 96 h. Exposure levels of Ninian WSF ranged from 0.16 to 2.50 ppm and those of condensate WSF ranged from 0.45 to 4.76 ppm. The main components in the exposure water were toluene and xylenes.

The threshold concentration of Ninian WSF which causes tainting in scallop adductor muscle was 0.5 ppm. The tainting threshold for condensate WSF was 0.8 ppm. The hydrocarbon level in the exposure water was a significant factor in the development of tainting, more so than the duration of exposure. There was a rapid reduction in the total hydrocarbon concentration in the adductor muscle in depurating scallops. The loss of taint was more gradual. Tainted scallops depurated after 24 to 264 hours in clean seawater, depending on the initial exposure level and the duration of exposure. The main components in tainted adductor muscle were toluene and xylenes. Selective accumulation of alkylated benzenes, naphthalene, and alkylated naphthalenes was observed, especially in those scallops exposed to the higher hydrocarbon levels. These may have contributed to the taint as well.

Analysis of the mixing ratios and the percentage of the original whole oil and condensate that remains dissolved suggests that tainting thresholds are unlikely to be achieved in the water column, especially near the seabed, during a short-term offshore blowout.

INTRODUCTION

Tainting is the development of an atypical flavour or odour in the edible tissues of finfish and shellfish, caused by natural spoilage or by the assimilation of contaminants. Tainting as a result of exposure to petroleum hydrocarbons has been documented frequently (see Tidmarsh *et al.*, 1985 for a review); however, most of the tainting cases have been related to industrial effluents or nearshore oil spills. Tainting as a result of offshore blowouts has been marginal (Whittle *et al.*, 1978). There is some evidence of tainting in flounder due to routine petroleum drilling activities (McGill *et al.*, 1987).

The potential for tainting in sea scallops (Placopecten magellanicus) has been examined in two recent studies. The first study, undertaken for Texaco

Canada Resources, involved experiments with the water-soluble fraction (WSF) of Ninian crude oil. The second study, carried out for Environment Canada, was concerned with tainting due to exposure to the WSF of Scotian Shelf natural gas condensate. The same experimental methodology was used for both studies (Ernst *et al.*, 1988a,b).

The purpose of the studies was to examine exposure time and concentration of the WSF of Ninian crude oil and Scotian Shelf natural gas condensate as factors in the development and persistence of tainting in sea scallops.

MATERIALS AND METHODS

Scallops were collected from Georges Bank and the Bay of Fundy and were kept at the National Research Council facility at Sandy Cove. Cumulative mortality over the holding period (three to four months in each case) was 5%. Exposures for tainting evaluation were conducted at Dalhousie University.

Figure 1 shows the configuration of the exposure system. The WSF was prepared in the large mixing vessel by stirring oil:water (1:99) and condensate:water (1:299) mixtures for 24 hours, followed by 48 hours of settling. The WSF was pumped directly through a head tank to each of three exposure tanks. Aerated diluent water was provided separately. The system was designed to allow a continuous flow at 1 L/min with the WSF and diluent seawater in the appropriate ratio to establish a known concentration of WSF in the exposure tanks. With the exception of the longest (96 h) exposures, the concentration of WSF in the exposure tanks could be maintained at a very steady level. Hydrocarbon concentrations were monitored at frequent intervals throughout the exposures with a fluorometer calibrated by gas chromatography. Exposure periods ranged from 3 h to 96 h. Depuration ranging from 24 to 264 h was also examined in scallops exposed to WSF. Exposure concentrations of Ninian crude oil WSF ranged from 0.16 ppm to 2.50 ppm and condensate WSF exposure concentrations ranged from 0.45 ppm to 4.76 ppm.

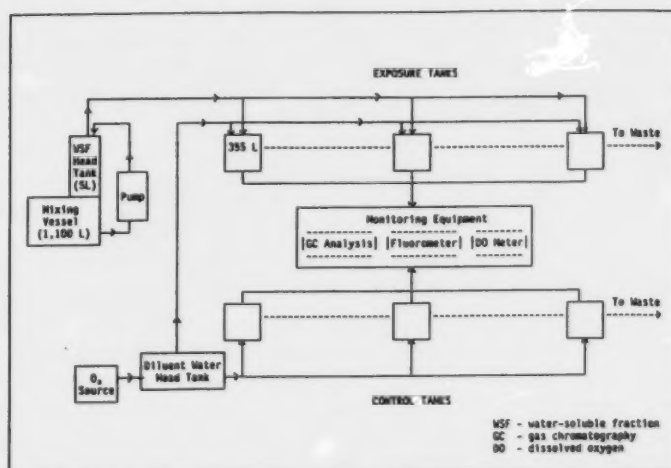


FIGURE 1. EXPOSURE SYSTEM CONFIGURATION FOR TAINING EVALUATION.

Exposure water and scallop adductor muscles were analyzed by gas chromatography with detailed identification of peaks by mass spectrometry. Exposure water was extracted using the Murray microextraction procedure (Murray, 1979). Hydrocarbons in the adductor muscles were extracted by using the steam distillation procedure of Ackman and Noble (1972). Although extraction recoveries were low for some of the more volatile hydrocarbons, the repeatability of extraction results was very good.

Figures 2 and 3 show the gas chromatograms of the WSF of Ninian crude oil and Scotian Shelf natural gas condensate, respectively. Concentrations of Ninian WSF in the mixing vessel ranged from 14 to 17 ppm. Concentrations of condensate WSF ranged from 42 to 56 ppm. The condensate was more soluble than the crude oil because of the higher concentration of aromatic compounds in the parent condensate stock. On the other hand, the WSFs of the crude oil and the condensate were quite similar in composition, as can be seen in the gas chromatograms. The percentage composition of the two WSFs is summarized in Table 1.



FIGURE 2. GAS CHROMATOGRAM OF STOCK WATER-SOLUBLE FRACTION OF NINIAN CRUDE OIL (14.3 PPM).

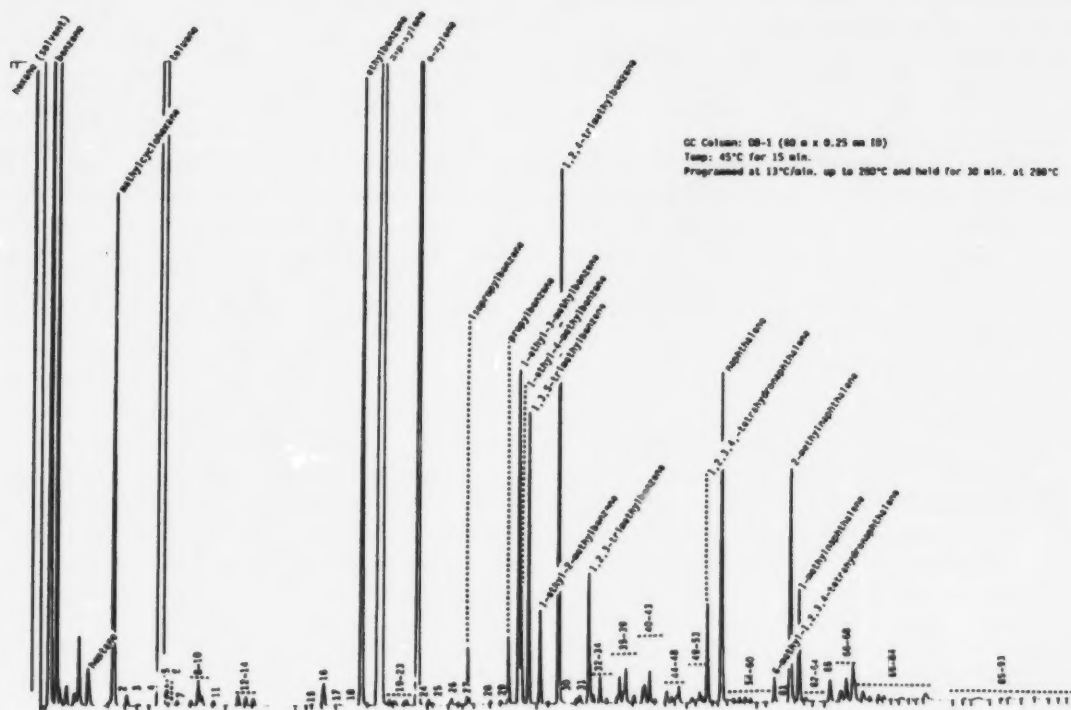
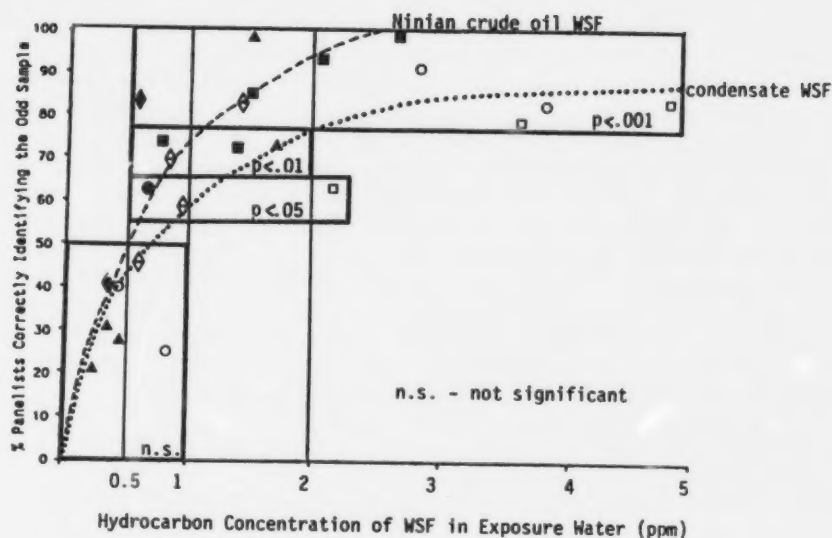


FIGURE 3. GAS CHROMATOGRAM OF STOCK WATER-SOLUBLE FRACTION OF SCOTIAN SHELF NATURAL GAS CONDENSATE (56 PPM).

TABLE 1. COMPOSITION OF NINIAN CRUDE OIL AND CONDENSATE WSF.

Component	Ninian Crude Oil WSF	Condensate WSF
benzene	34.3%	16.0%
toluene	39.3%	51.4%
ethylbenzene	1.7%	2.0%
xylene	8.3%	20.2%
alkylated benzenes	2.7%	3.5%
naphthalene	0.1%	1.2%
alkylated naphthalenes	0.7%	1.2%
larger aromatics	2.9%	0.1%
others	10.0%	4.4%

The similar composition of the WSFs suggests that the results of exposure and tainting evaluation should be similar. This is in fact the case, as can be seen in Figure 4, which shows the relationship between the hydrocarbon concentration in the exposure water and the degree of tainting (expressed as the percentage of panelists correctly identifying the odd sample).



Exposure Time (hours)	condensate WSF	Ninian crude WSF
3	○	●
24	□	■
48		▲
96	◊	◆

FIGURE 4. RELATIONSHIP BETWEEN THE DEGREE OF TAINING IN SCALLOP ADDUCTOR MUSCLE AND THE HYDROCARBON CONCENTRATION IN THE EXPOSURE WATER (LEVELS OF SIGNIFICANCE REFER TO DEGREE OF TAIN).

The threshold level of Ninian crude oil WSF which causes tainting in scallops during short-term exposure is 0.5 ppm. The threshold for condensate WSF is 0.8 ppm for equivalent exposures. There was a consistent increase in the degree of tainting with increasing exposure concentration. This relationship was most apparent near the tainting threshold (0.5-0.8 ppm exposure concentration) and flattened out as the tissues became more infused with hydrocarbons. Obviously, the tainting threshold depends on some aspect of scallop metabolism involved in uptake and excretion of hydrocarbons. Below the tainting threshold, scallops apparently maintain an equilibrium between continuous dosing and excretion of the hydrocarbons such that the adductor muscle is not flooded with those compounds which cause tainting. Above the threshold exposure level, the metabolic process involved in hydrocarbon excretion may not work in equilibrium and accumulation of hydrocarbons in the adductor muscle must occur, resulting in tainting. Within the exposure times that were examined (3-96 h), there was a suggestion that increasing the exposure duration for a specific exposure concentration below 1 ppm increased the degree of tainting by a small amount.

The tissue analysis indicated that the actual hydrocarbon level in adductor muscles which were tainted exceeded 0.01 ppm for scallops exposed to Ninian WSF and 1.25 ppm for scallops exposed to condensate WSF.

Figures 5 to 8 show the depuration curves for tainting and hydrocarbon levels in the adductor muscle of scallops exposed to Ninian WSF and condensate WSF. The most obvious common feature of the two data sets is the rapid reduction of the total hydrocarbon burden in the adductor muscle once in clean seawater (approximately 90% reduction within 24 hours). The reduction in the degree of tainting was not as rapid, implicating one or more compounds as the cause of tainting, rather than the total hydrocarbon burden. Scallops exposed to a low concentration of Ninian WSF (1.4 to 2 ppm) for 24 hours were clear of a taint after 76 to 168 hours of depuration. Scallops exposed to 2.66 ppm condensate WSF for 24 hours were clear of a taint within 24 hours of depuration. Those exposed to lower concentrations (0.92 ppm) for a longer period (96 h) required 96 to 264 hours to clear of a taint.

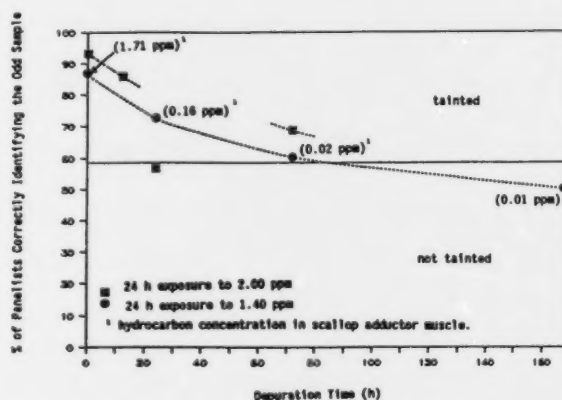


FIGURE 5. RELATIONSHIP BETWEEN TAINING IN SCALLOPS EXPOSED TO NINIAN CRUDE OIL WSF AND DEPURATION TIME.

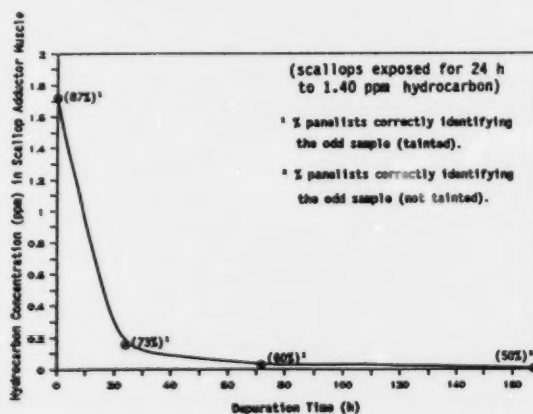


FIGURE 6. RELATIONSHIP BETWEEN HYDROCARBON CONCENTRATION IN THE ADDUCTOR MUSCLE OF SCALLOPS EXPOSED TO NINIAN CRUDE OIL WSF AND DEPURATION TIME.

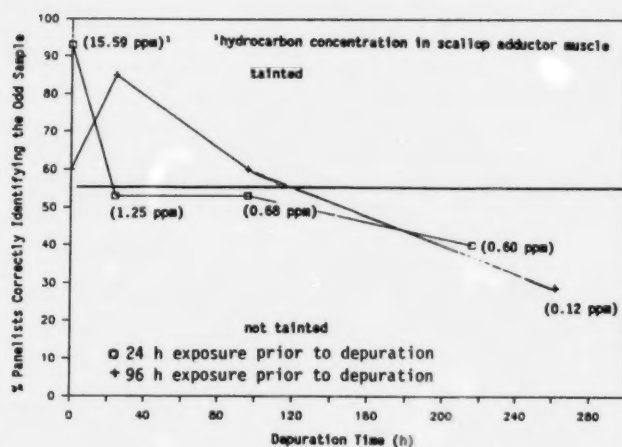


FIGURE 7. RELATIONSHIP BETWEEN TAINING IN SCALLOPS EXPOSED TO CONDENSATE WSF AND DEPURATION TIME.

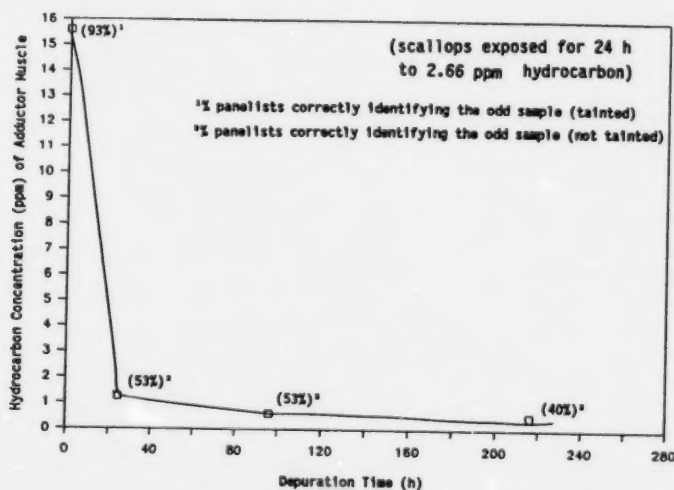


FIGURE 8. RELATIONSHIP BETWEEN HYDROCARBON CONCENTRATION IN THE ADDUCTOR MUSCLE OF SCALLOPS EXPOSED TO CONDENSATE WSF AND DEPURATION TIME.

Figures 9 and 10 show the hydrocarbon composition of scallop adductor muscles tainted with Ninian WSF and condensate WSF. The chromatograms show most of the main constituents which were present in the exposure water. Toluene and xylenes were the most prominent hydrocarbons in tainted adductor muscle. They were absent in adductor muscle which had depurated free of a taint. These compounds have been implicated in tainting in previous studies (see Ernst *et al.*, 1988a for a review). The relatively high levels of alkylated benzenes, naphthalene, and alkylated naphthalenes also implicate these compounds, although only at the higher concentrations, since low levels of these compounds were retained in adductor muscle which was free of a taint.

TABLE 2. ACCUMULATION OF HYDROCARBONS IN SCALLOP ADDUCTOR MUSCLE EXPOSED FOR 24 H TO CONDENSATE WSF.

Hydrocarbon Exposure Level (ppm)	Hydrocarbon Tissue Level (ppm)	Level of Significance of Taint	Total ¹ Hydrocarbon Accumulation	Hydrocarbon Accumulation Factors ²								
				toluene	m+p xylene	o-xylene	alkylated benzenes and others Peaks 44-53	naphthalene	2-methyl-naphthalene	dimethyl-naphthalene and others Peaks 62-73	trimethyl-naphthalene and others Peaks 74-81	PNAH
0.45	0.70	not significant	1.6	.5	.9	.2	.7	2.3	2.3	.7	5.6	0.5
0.78	1.38	not significant	1.8	.5	.9	1.5	1.9	3.7	5.3	8.1	9.1	0.9
2.66	15.59	p <.001	5.9	.4	.8	1.1	14.0	4.9	20.0	44.5	25.0	7.5
3.79	48.77	p <.001	12.9	.6	1.2	1.4	14.0	6.1	19.0	26.0	7.5	5.0

¹Tissue level divided by exposure level.

²The ratio of the individual hydrocarbon concentration to the total hydrocarbon concentration in the adductor muscle divided by the equivalent ratio in the exposure water.

TABLE 3. RETENTION OF HYDROCARBONS IN SCALLOP ADDUCTOR MUSCLE WHICH HAD BEEN EXPOSED FOR 24 H TO 2.66 PPM HYDROCARBON FOLLOWED BY A DEPURATION PHASE - INITIAL ADDUCTOR MUSCLE HYDROCARBON CONCENTRATION 15.59 PPM.

Depuration Time (h)	Level of Significance of Taint	Total ¹ Hydrocarbon Retention	Hydrocarbon Retention Factors ²								
			toluene	m+p xylene	o-xylene	alkylated benzenes and others Peaks 44-53	naphthalene	2-methyl-naphthalene	dimethyl-naphthalene and others Peaks 62-73	trimethyl-naphthalene and others Peaks 74-81	PNAH
24	not significant	0.08	.07	.3	.3	.6	.6	.6	.7	5.1	5.3
96	not significant	0.04	.07	.1	.3	.5	.3	.2	1.2	3.8	5.9
216	not significant	0.04	.08	.1	.3	2.1	.3	.2	1.2	6.7	6.7

¹Hydrocarbon level in depurated adductor muscle divided by hydrocarbon level in adductor muscle which was not depurated.

²The ratio of the individual hydrocarbon concentration to the total hydrocarbon concentration in the depurated adductor muscle divided by the equivalent ratio at time 0 (not depurated).

These tainting data are only useful if they can be extrapolated to a field situation in which tainting is a concern. The difficulty in extrapolating laboratory data on tainting to a real oil spill or blowout situation lies in the comparison of the WSF responsible for tainting in the laboratory with what is usually reported as whole oil or condensate under a slick. This problem can be dealt with by examining the percentage of whole oil or condensate that remains as a true WSF, calculating the concentration of whole oil or condensate which must be sustained in the water column to produce a tainting threshold of WSF, and then comparing the required concentration of whole oil or condensate to concentrations that have been observed or calculated in the past.

Examination of the mixing ratios indicated that no more than 1.7% of the original whole condensate volume and 0.2% of the original Ninian crude oil remained as a stable WSF. There was some evidence that reducing the mixing ratio (decreasing the volume of oil or condensate in a given volume of seawater) resulted in a larger percentage of the original volume remaining as WSF. When extrapolated to a real spill or blowout situation, with mixing ratios of 1:10,000 to 1:1,000,000, the percentage dissolved could theoretically range between 4 and 8% for condensate and about 0.5 to 1% for crude oil. Assuming a tainting threshold of 0.8 ppm, the concentration of whole condensate which must be sustained in the water column for at least 3 hours to cause tainting in scallops exceeds 10 ppm. The equivalent value for Ninian crude oil (with a tainting threshold of 0.5 ppm) is greater than 50 ppm.

According to studies by Ross (1982), the maximum initial concentration of whole condensate during a blowout would not exceed 8.5 ppm. The concentration would be rapidly reduced over time (with no further input of condensate) and away from the location of the blowout. Accordingly to McAuliffe (1986), sustained whole oil-in-water concentrations under naturally dispersed oil slicks are less than 1 ppm. Thus, it can be concluded from this simple analysis that an oil or condensate WSF tainting threshold is unlikely to be achieved in the water column near the seabed during a short-term spill or blowout, and the risk of tainting in scallops is low. Other factors which have not been fully examined could lead to other conclusions. For example, long-term exposure (greater than 96 h) to dissolved fractions of oil at a concentration below the short-term tainting threshold could cause a taint in scallops. This should be examined in future tainting studies.

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ACUTE TOXICITY OF PETROLEUM HYDROCARBONS TO THE ARCTIC LITTORAL MYSID, *MYTIS OCLATA* (FABRICIUS)

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ABSTRACT

Acute lethal toxicity tests were conducted with young-of-the-year *Mytis oculata* exposed to oil-in-water dispersions (OWDs) and water-soluble fractions (WSFs) of Norman Wells crude oil. Median lethal concentrations (96-h LC50s) are among the lowest reported for arctic marine crustaceans, ranging from 0.49-0.62 mg/l for WSFs and 4.51-7.57 mg/l for OWDs. OWDs in sealed containers were more toxic to mysids than in open ones. The retention of volatile hydrocarbons in test solutions caused behavioral abnormalities and latent toxic effects at concentrations lower than the LC50. Adverse effects were caused primarily by the chemical toxicity of water-soluble aromatic compounds since there were no apparent physical effects due to dispersed oil droplets. The water-soluble component of OWDs was more toxic than WSFs. Due to its sensitivity, its vulnerability, its availability in nearshore waters, and its ease of maintenance under laboratory conditions, *M. oculata* is recommended as a test organism for arctic marine toxicity testing and environmental monitoring.

INTRODUCTION

Oil exploration in Arctic waters over the past two decades has raised concerns about the effects of oil pollution on the arctic ecosystem. The relative environmental impact of an oil spill in polar seas will likely be far greater than that of a comparable one in temperate seas for reasons that have been described by Percy and Wells (1984). In order to predict the ecological impacts of oil spilled in arctic waters, more research is needed on the basic biology and physiological sensitivity of the ecologically important species. A number of arctic marine species have already been tested (Percy and Wells 1984; Wells and Percy 1985), but the coverage is still sparse. This study examines the effects of petroleum hydrocarbons on the littoral mysid, *M. oculata*.

Littoral mysids are important secondary producers in many estuarine and marine food webs (Mauchline 1980). In the arctic and subarctic *M. oculata* is an important food item for marine birds, fish and mammals, including commercially important species such as arctic charr (*Salvelinus alpinus*) and ringed seal (*Phoca hispida*) (Dunbar 1941; Grainger 1953; McLaren 1958; Bradstreet 1980; Green 1983; Smith 1987). During the open water season, large dense shoals of *M. oculata* are usually found associated with beds of macroalgae in the subtidal zone (i.e. less than 50 m deep). In Frobisher Bay, young-of-the-year mysids migrate into the intertidal zone during flood tides. They are hypobenthic during the day but migrate to the surface waters at night (Kaufman 1979). In the winter, *M. oculata* has been found associated with the under-ice

surface in water depths of 12 to 18 m at 0.3 to 0.6 km from shore (D. Pike, pers. comm.).

Such sub-littoral and sub-ice habitats are highly vulnerable to oil pollution (Percy and Wells 1984; Wells and Percy 1985). Spilled oil often strands on beaches and is incorporated rapidly into sediments. Weathering can be slow and oil can remain buried in intertidal beaches, releasing water-soluble aromatic hydrocarbons for many years. The sub-ice habitat may be even more vulnerable to spilled oil. Oil spilled beneath the ice accumulates rapidly at the ice-water interface. Ice-cover greatly reduces evaporation (Payne and McNabb 1984) and more toxic volatile fractions are released into the water. During fall and winter, oil becomes encapsulated in the growing ice sheet and is released into the water again during spring, when biological activity is near its peak.

Mysis oculata populations in the Arctic are clearly vulnerable to spilled oil, but whether they are physiologically sensitive to it is another question. Mysids living in temperate waters have been shown to be exceptionally sensitive to petroleum hydrocarbons (Anderson et al. 1974a; Wells 1982; Laughlin and Linden 1983; Smith and Hargreaves 1984). Two arctic littoral mysids, *Mysis litoralis* and *Mysis relicta* are also killed by exposure to low levels of oil (Schneider 1980; Carls and Korn 1985). However, the physiological sensitivity to oil of *Mysis oculata* has up to now not been examined. In this study, acute toxicity tests were carried out to determine the sensitivity and behavioral responses of *Mysis oculata* exposed to oil-in-water dispersions and water-soluble fractions of a northern crude oil.

MATERIALS AND METHODS

Collection and maintenance of animals

In August 1986 and 1987, young-of-the-year *M. oculata* were collected by dip-net from a sheltered embayment in upper Frobisher Bay, N.W.T., Canada (63° 44'N, 68° 31'W). They were transported in cold seawater ($T = 0-20^{\circ}\text{C}$) to the Iqaluit Research Laboratory and transferred to 9-L polystyrene containers of clean seawater ($T = 0^{\circ}\text{C}$, $S = 32$ ppt) until shipping. Live mysids were flown to the Arctic Biological Station (ABS) in insulated containers. Total transit took less than 7 hrs and there was no mortality. At the ABS, animals were kept in three 65-L holding tanks containing re-circulated artificial seawater (Instant Ocean(TM), $T = 1.5 \pm 1.0^{\circ}\text{C}$, $S = 33.0 \pm 1.0$ ppt, $\text{pH} = 7.9$). The light intensity was 6 $\mu\text{Einsteins m}^{-2}\text{s}^{-1}$ (or 60 lux) and the photoperiod was similar to that of Frobisher Bay. The mysids were fed dried fish food (Cora Feed(TM)) ad libitum every 2-3 d.

Toxicants

Two different batches of Norman Wells crude oil (July 1983 and July 1986) and one reference toxicant (phenol) were used. Oil used for oil-in-water dispersions (OWD) was stored in tightly-capped 14-ml glass vials in a dark incubator at 0°C . Oil used for the preparation of water-soluble fractions (WSF) was transferred to 500-ml glass erlenmeyer flasks and similarly stored.

Norman Wells crude is a light oil with a relatively high percentage (i.e. 60-65%) of volatile hydrocarbons below $n\text{-C}_{12}$ (Fig. 1). Typically, it has a pour point of -50°C , a specific gravity of 0.833 at 16°C , and a

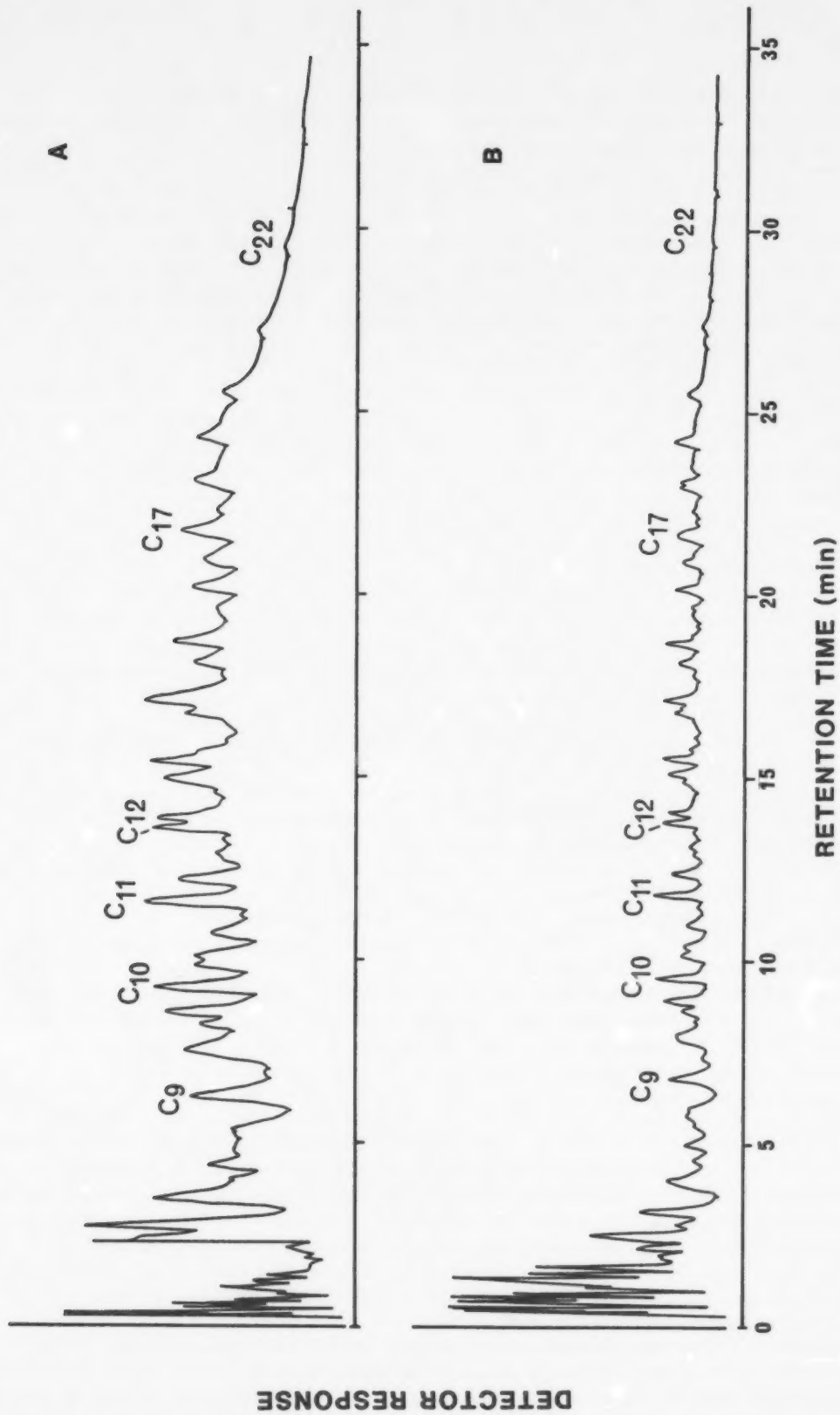


Fig. 1. Gas chromatograph traces of Norman Wells crude oils. A: July 1983 oil; B: July 1986 oil.

viscosity of 6.5 at 160C centipoise (Keevil and Ramseier 1975). A comparison of GC profiles (Fig. 1) indicates that the July '83 oil former has almost double the proportion of high molecular weight alkanes (C17 - C22) than the July '86 oil (i.e. 12.19% vs 6.71%), and slightly less volatile hydrocarbons (i.e. 60.81% vs 64.25%). Also, the lighter '86 oil is a more diverse mixture of compounds. Additional quantities of each batch of oil are available for testing by interested investigators.

Reagent grade phenol served as a reference toxicant to compare the sensitivities of the two different collections of mysids used in this study (i.e. 1986 vs 1987). Phenol is commonly found in crude oils (Posthuma 1977), and has been recommended as one reference toxicant for bioassays (Klaverkamp et al. 1975; Fogels and Sprague 1977; P.G. Wells, pers. comm.).

Preparation of test mixtures

Toxicant solutions were prepared in filtered (Whatman(TM) in-line filter, 1 μ m) Instant Ocean(TM) artificial sea-water (S = 32 ppt), aerated and cooled to 0-20C. During preparation, all solutions were kept sealed at 0-20C to minimize evaporation.

OWDs were prepared with July '83 oil using methods similar to Percy and Mullin (1975) and Foy (1978). A given amount of oil (i.e. 5, 10, 15, 20, 30 or 40 μ l) was added to 550 ml of filtered seawater in a 750-ml wide-mouth glass jars. The jars were capped and shaken vigorously on a reciprocating shaker at 280 oscillations/minute for 30 min and the solutions allowed to settle in 500-ml separatory funnels for 90 min. The lower 425 ml of this "semi-stable dispersion" (Percy and Mullin 1975) was drained into a 2-L erlenmeyer flask, hand-stirred, subsampled for hydrocarbon analysis, and transferred to test jars.

WSFs were prepared by the method of Anderson et al. (1974a). The stock WSF was then diluted with filtered seawater to prepare a series of 6 toxicant concentrations (i.e. 5, 15, 25, 35, 45, and 60%).

Phenol was prepared by diluting a stock solution of 10 g/l with seawater. Five or six concentrations were prepared in the range of 5 to 125 mg/l. The mixtures were stirred with a glass rod and the jars were sealed until the animals were added. Phenol concentrations are expressed as nominal amounts added to seawater.

Each toxicity test included 3 to 6 concentrations of toxicant and a control solution containing only filtered seawater. All solutions were replaced daily with fresh mixtures.

Hydrocarbon analyses

Preliminary results of WSF mixtures by fluorescence spectroscopy yielded results showing a high degree of variance among replicate samples. Overall precision was low, possibly due to losses of volatile hydrocarbons during the solvent concentration step (Warner et al. 1980). Hence, the more accurate gas chromatographic technique described below was used to analyze WSFs.

The method of Keizer and Gordon (1973) was used to measure the concentration of total fluorescing hydrocarbons in OWDS. During toxicity tests, 115-ml subsamples of the test solutions were taken at 0 h and 24 h. They were kept in tightly-sealed 125-ml glass serum bottles and stored at 00C for 1 to 2 hours. Before extraction with spectrophotometric grade dichloromethane, each subsample was vigorously hand-shaken to re-disperse oil which may have settled at the water surface. Subsamples were extracted twice with 10 ml of dich-

loromethane and the extracts were stored in tightly capped glass culture tubes until the evaporation step (i.e. 1-2 weeks). Following evaporation under vacuum at 310C, the residues were dissolved in 10 ml of spectrophotometric grade hexane, stored in glass culture tubes and kept at -200C until further analysis. Preliminary experiments demonstrated that these storage methods did not affect the fluorometric readings of oil-in-hexane samples. Fluorescence was measured in a Turner Model 430 Spectrofluorometer with a slit width of 15 nm at optimum excitation (370 nm) and emission (385 nm) wavelengths. The oil concentration was estimated from a calibration curve ($r > 0.9$) prepared with 6 standards of known concentration. Readings were corrected for seawater blanks.

Gas chromatography was used to determine the concentrations of total volatile hydrocarbons (C6 to C10, or benzene to C3-naphthalene) as well as the composition of WSF and OWD mixtures. Eight 1-L samples consisting of 0-h and 24-h-old OWDs and WSFs were prepared separately from toxicity tests. Samples of OWD were settled for 48 hrs to insure the separation from solution of most particulate hydrocarbons (i.e. C12 alkanes and up), thus producing a stable water-soluble fraction (Lockhart et al. 1984). A small amount of sodium azide was added to each sample to prevent bacterial degradation. Samples were kept refrigerated (at about 50C) in tightly capped 1-L glass bottles wrapped in aluminum foil until analysis. A method of GC analysis originally designed to analyze volatile organic compounds in fish tissues (Murray and Lockhart 1988) was used. The technique, which combines the principles of purge and trap, has now been successfully applied to water samples with recovery rates in the range of 80-98% for 8 common volatile hydrocarbons (D. Murray, pers. comm.). The identification of peaks on the GC traces were confirmed by gas chromatography/mass spectrometry applied to one oil-in-water sample.

Test procedures

An acclimation period of at least 10 d preceded experimentation. Forty-eight hrs prior to testing, 80 to 100 animals were transferred to smaller holding tanks and starved. Median lethal concentrations (LC50s) and median effective concentrations (EC50s) were determined by standard acute 96-h lethal toxicity tests (American Public Health Association 1980). All experiments were conducted from Sept. '86 to Feb. '87 and from Sept. '87 to Dec. '87.

Mysids were exposed to semi-static (i.e. replaced daily) toxicant mixtures for 96 hrs and then transferred to clean seawater for 48 hrs to test for post-exposure recovery and latent effects (Hansen and Kawatski 1976; Wright 1976). Animals were assigned to test jars randomly as recommended by Sprague (1969). The time between the addition of the first animal and the last one was always less than 1 h. Most tests were conducted using 750-ml wide-mouth glass jars with 670 ml of solution and 5 mysids per jar (organism loading = 0.17 g/l). However, a series of OWD tests used 1-L glass beakers, each containing 10 animals (loading = 0.23 g/l). In all replicate tests, 10 animals were used at each concentration.

Table 1 summarizes the experimental methods used in this study. For each toxicant, sealed jar tests were conducted in which 750-ml jars were sealed with a screw cap lined with aluminum foil. In tests with 1-L beakers, these were sealed with foil only. In all cases there was an air space of 1 cm between the cap and the water surface. Open-jar tests were conducted with OWDs using both 750-ml jars and 1-L beakers. All exposure jars were kept in an incubator at 00C. A "cool white" fluorescent light illuminated the jars at an intensity of about 1 μ einstein $m^{-2}s^{-1}$ (10 lux) for 10 hrs per day.

TABLE 1. Summary of the toxicity tests conducted and the experimental methods used.

Test No.	Date	Mysid collection year	Toxicant	Open or sealed jars	No. of animals per jar	Size of jar (ml)	No. of concentrations tested	No. of tests conducted
1-2	09/86	1986	OWD83 ¹	OPEN	5	750	5	2
3-7	10/86	1986	OWD83 ¹	OPEN	10	1000	4	5
8-12	12/86	1986	PHENOL	SEALED	5	750	6	5
13-17	01/87	1986	OWD83 ¹	SEALED	10	1000	2-3	5
18-21	09/87	1987	PHENOL	SEALED	5	750	5	4
22-23	10/87	1987	WSP83 ²	SEALED	5	750	6	2
24-27	10/87	1987	WSP86 ³	SEALED	5	750	6	4
28	11/87	1987	OWD83 ¹	SEALED	5	750	6	1

1 - Oil-in-water dispersion prepared with oil from the July '83 batch.

2 - Water-soluble fraction prepared with oil from the July '83 batch.

3 - Water-soluble fraction prepared with oil from the July '86 batch.

Death and four behaviors of *M. oculata* exposed to oil-water mixtures were defined as follows:

- A - Animal in normal upright position; walking or swimming; no loss of equilibrium.
- B - Loss of equilibrium; animal lying on dorsal or lateral side; more than half of the thoracic appendages moving.
- C - Animal lying on dorsal side; less than half of the thoracic appendages moving.
- D - Visible motion only after gentle prodding with a glass rod.

DEATH - No visible motion after prodding with a glass rod.

During exposure to toxicants and controls, observations of behavior, death, molting and cannibalism were generally made after 2, 5, 10, 24, 30, 48, 54, 72, 78 and 96 hrs. Animals were then observed 24 and 48 hrs after their transfer to clean seawater. The behaviors of the animals were assessed for 30 s. Molts and dead animals were removed.

Several parameters of the toxicant mixtures and control seawater were monitored regularly during experiments (Table 2). The water quality during the test remained favorable according to APHA (1980) standards.

Statistical Methods

Exposure concentrations for OWD and WSF tests are expressed as the means of measured concentrations at 0 h and 24 h. In the case of OWDs measured by fluorescence spectroscopy, geometric means are used since dispersed oil concentration under such conditions decrease exponentially over a 24-h period (Percy and Mullin 1975; Wells and Sprague 1976). Student's t-test (SAS 1985) was used to determine the statistical differences between arithmetic means.

Median lethal concentrations were calculated from the percentage of animals which died during 96-h tests. Median effective concentrations were calculated for abnormal behavioral stages (i.e. B, C, and D) using the percentage of individuals exhibiting the behavior under study as well as behaviors indicative of progressive deterioration in health. For example, EC50s for stage B were calculated using the percent animals exhibiting stages B, C, D and DEATH. Hence, the EC50 value corresponds to the concentration which causes a stage B or "worse" in half of the animals tested.

Data obtained from post-exposure treatments in clean seawater were used to calculate EC50s for "moribundity" and "ecological death". Animals which died during the post-exposure period were considered to have been moribund and therefore counted as dead within the 96-h test, as suggested by Rice et al. (1977). "Ecologically dead" animals were defined as those which did not fully recover to stage A within the post-exposure period and, therefore, may die because of increased vulnerability to environmental stresses and/or predation (Rice et al. 1977).

LC50s, EC50s, their confidence limits and slope functions were calculated using three different methods: probit analysis (Finney 1971), the moving average method (Bennet 1952), and the binomial test (Siegel 1956). Moving average results are not reported because they are similar to probit results and hence, did not yield useful additional information. Binomial test results are reported as a supplement to probit results but they are not used in statistical comparisons. Dose-response data analyzed by the probit method

TABLE 2. Summary of water parameter measurements for toxicity tests with *M. oculata*.

Parameter measured	Mean	S.D.	n	Measurement method
Temperature (°C)	0.6	0.7	320	Wahl ^(TM) platinum 392M digital heat-prober
Salinity (ppt)	31.0	1.0	9	Goldberg ^(TM) T/C refractometer (Model 10419)
pH	7.86	0.06	6	Radiometer ^(TM) PHM63 digital pH-meter
Carbonate alkalinity (meq/l)	2.45	0.004	7	Parsons et al. (1984)
Ammonia (µg at NH ₃ -N)	5.8	3.4	14	Dal Pont et al. (1974)
Dissolved oxygen (ml/l)	5.7	0.5	8	Orbisphere ^(TM) microprocessor oxygen indicator (Model 2609) + oxygen electrode
Dissolved oxygen (% saturation)	77.1	6.4	4	As above

were corrected for control mortality/behavioral changes by using Abbott's formula (Finney 1971). All calculations were performed using two BASIC computer programs supplied by C. Stephan (U.S.E.P.A., Duluth, MN). Statistical differences between probit LC50s (or EC50s) were tested at the 5% level of significance by the formula for Standard Error of the Difference, as used in Litchfield and Wilcoxon (1949).

RESULTS

Hydrocarbon analyses

Fluorescence spectrophotometry. In the four series of tests conducted, the means of most 0-h concentrations increased significantly with the amount of oil added to test jars. Overall, the results of three concentrations were discarded because their initial means were not statistically different ($P > 0.05$) from those of bracketing concentrations. Overlap between concentrations probably occurred due to the unstable nature of oil in water and the narrow intervals between the volumes of oil added (i.e. 5 or 10 $\mu\text{l/l}$). Over a 24-h static period, the concentration of dispersed oil decreased significantly, mostly due to oil droplets coalescing and rising to the surface (Anderson et al. 1974a; Percy and Mullin 1975). The percentage of oil lost from the water ranged from 25.1 to 77.5%, with an overall mean of 58.4% (s.d. = 11.9%). Some of this loss may also be attributable to other factors such as volatilization, uptake by organisms, microbial degradation and photochemical oxidation. Although OWDs were unstable under the conditions used in this study, geometric means are believed to be a reliable estimate of exposure concentrations.

Gas chromatography. An examination of the GC traces of both WSF and OWD mixtures revealed that most of the major peaks of volatile hydrocarbons in the aqueous phase were aromatic compounds, primarily alkylated benzenes and naphthalenes (Fig. 2). All of these fractions are known for their toxicity to marine crustaceans, especially the naphthalenes (Anderson et al. 1974a; Tatem et al. 1978; Abernethy et al. 1986). All mixtures had similar compositions but certain compounds occurred in different proportions depending on the sample. Overall, the most obvious difference occurred between fresh OWDs and WSFs; the former contained a higher proportion of volatile hydrocarbons from ethylbenzene to C3-naphthalene and a major unresolved envelope of low molecular weight and high molecular weight hydrocarbons (Fig. 2).

Total volatile hydrocarbon concentrations were determined for OWD and WSF mixtures (Table 3). Both WSFs prepared without animals had a similar composition, however, the WSF86 mixture had a slightly higher concentration of aromatic hydrocarbons as well as a higher percentage of oil lost in 24 hrs. These results may reflect the composition of each crude oil. When mysids were added to the test jars, the average percent oil loss was increased by about 20%, suggesting that *M. oculata* take up a significant portion of dissolved volatiles. Both OWDs and WSFs had a similar initial (0-h) concentration of volatiles, but OWDs had the lowest mean concentration due to relatively high losses during a 24-h period. The average percent loss for OWDs in open jars was about 17% higher than in sealed jars. Sealing test jars was an efficient method for retaining at least 70% of the volatile hydrocarbons contained in OWD mixtures and at least 85% of those in WSFs. This method of control has been recently used by Abernethy et al. (1986).

The concentrations of volatile hydrocarbons for all dilutions used in toxicity tests were calculated as percentages of the average concentration of

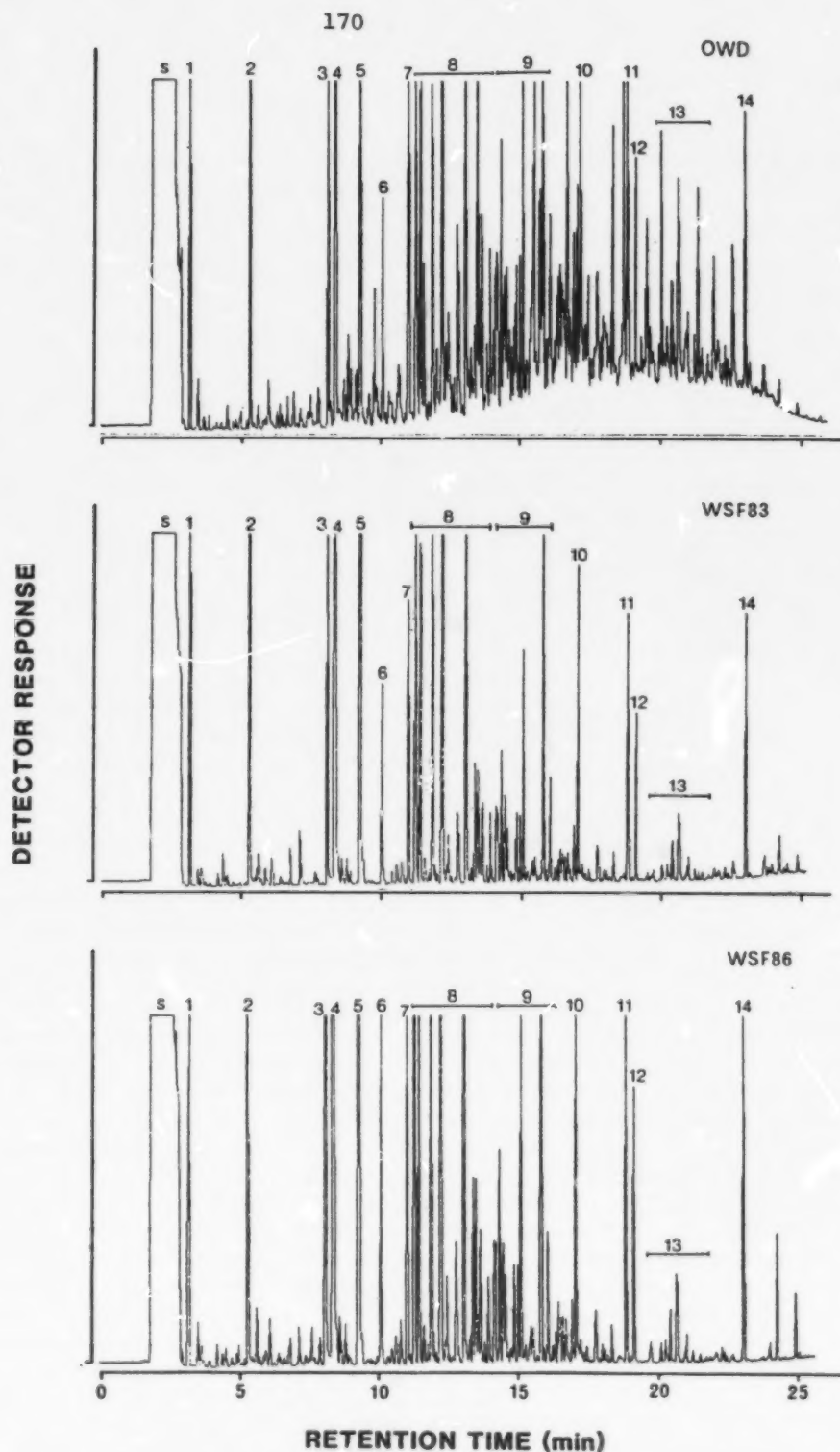


Fig. 2. GC traces showing volatile hydrocarbon compounds contained in Norman Wells crude oil-in-water mixtures. S= carbon disulfide solvent; 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*- + *p*- xylene; 5 = *o*- xylene; 6 = iso-propylbenzene; 7 = *n*- propylbenzene; 8 = C₃-alkylated benzenes; 9 = C₄-alkylated benzenes; 10 = naphthalene; 11 = 2-methyl-naphthalene; 12 = 1-methyl-naphthalene; 13 = C₂-alkylated naphthalenes; 14 = internal standard (*n*-decyl benzene)

TABLE 3. Concentrations of volatile hydrocarbons in oil-water mixtures as determined by gas chromatography.

Toxicant	Total volatile hydrocarbons ($\mu\text{g/l}$)			Average % oil loss
	0-h	24-h	Mean 0-h + 24-h	
WSP83 ¹	1110.7	1009.7	1035.6	8.1
	1047.5	974.4		
WSP86 ¹	1293.8	1131.1	1174.9	15.3
	1250.1	1024.6		
WSP86 ¹ + 5 nysids	1293.8	817.8	1040.6	36.4
	1250.1	800.5		
OWD83 ²	1103.4	578.2	823.2	45.9
	1033.4	577.7		
OWD83 ³	1103.4	766.0	913.0	29.1
	1033.4	749.0		

1 - 60% of stock WSP; sealed jars.

2 - 60 mg/l of oil added; open jars.

3 - 60 mg/l of oil added; sealed jars.

each toxicant sample measured by gas chromatography. Only concentrations measured from samples without animals were used in the calculations.

Toxicity tests

Most LC50s and EC50s of different exposure times (i.e. 2 to 96 hrs) were not statistically different because of overlapping confidence limits. Therefore, incipient LC50s and EC50s could not be calculated from toxicity curves and test results are presented as several 96-h LC50s and 96-h EC50s, or as a range.

Although control mortality/behavioral changes occurred in 2 out of 28 toxicity tests, corrected dose-response data were not used in statistical comparisons of LC50s and EC50s. Since control mortality (or effect) was inconsistent and below 10% (i.e. representing one weak organism in a group), the test is valid and correction of the LC50 (or EC50) for this mortality (or effect) would seem to be a meaningless exercise (Doudoroff et al. 1951; Sprague 1973; Stephan 1977). Preliminary calculations showed that the use of corrected data did not significantly change the statistical results obtained with non-corrected data.

Mysid length and parasitism. Mysids from the two different collections differed in their mean lengths and percent parasitism. Animals sampled in 1986 had a statistically greater mean total length ($P < 0.0001$) and twelve times more parasitized individuals than those of 1987. The epicarid isopod, *Dajus mysidis*, was the most visible parasite and was usually found attached to the last thoracic somite of the mysid, on the ventral surface (also see Tattersall and Tattersall 1951). In some cases, ciliates were seen swimming on the body surface of dead mysids.

Phenol. To compare the sensitivity of mysid collections the 96-h LC50s and 96-h EC50s for moribundity and "ecological death" were compared (Table 4). Although the two groups differed in their mean length and percent parasitism, they did not differ in their sensitivity to phenol. There was significant overlap in the ranges of LC50s, EC50s and their confidence limits. LC50s and EC50s for all toxicity tests were compared under the assumption that both stocks of mysids were equally sensitive to oil-in-water mixtures.

Oil-in-water dispersions. The 96-h LC50s of mysids exposed to OWDs ranged from 4.51 to 7.57 mg/l, using four different experimental methods. To eliminate bias due to the potential effect of jar size on animal sensitivity, only tests conducted with the same size jars were statistically compared. Mysids held in 1-L beakers as opposed to 750-ml jars, were more crowded and may have been more sensitive partly due to stress rather than solely due to the sealing of test jars. In tests with 750-ml jars, LC50s and EC50s were consistently 1-3 mg/l lower when jars were sealed (Fig. 3). There were no statistical differences between the LC50s, but as a result of prolonged exposure to volatile hydrocarbons certain EC50s for sealed-jar test (i.e. method no. 4) were statistically lower than comparable EC50s obtained using the open-jar method (Fig. 3). In tests with 1-L beakers there was no statistical difference between the LC50s of sealed- and open-jar tests. The similar toxicity of both mixtures may have been caused by losses of volatile hydrocarbons from sealed beakers due to their aluminum covers not providing an airtight seal. EC50s for all OWD tests were lower than LC50s, with stages B and "ecological death" producing the lowest values. Method no. 4 had the lowest EC50 values (i.e. 1.54 - 2.73 mg/l) and most of these were statistically different from the LC50. Differences in LC50s and EC50s due to jar size were small (i.e. 1-2 mg/l) and not statistically different.

TABLE 4. Ranges of 96-h LC50s, 96-h EC50s and their confidence limits for two different collections *M. oculata* exposed to phenol.

Calculation method	Stage	Mysid collection year	No. of tests	Range of 96-h LC50s or EC50s ¹ (mg/l)	Range of confidence limits
Probit	DEATH	1986	4	37.8 - 75.0	26.4 - 107.8
		1987	2	37.2 - 56.1	22.7 - 104.8
	MOR24 ²	1986	4	29.8 - 71.2	19.3 - 98.8
		1987	3	25.8 - 36.9	13.1 - 60.8
Binomial	DEATH	1986	5	50 - 89	5 - 125
		1987	4	35 - 74	5 - 125
	MOR24 ²	1986	5	25 - 69	5 - 125
		1987	4	21 - 40	5 - 125
	EC024 ³	1986	5	11 - 23	5 - 125
		1987	4	8 - 10	5 - 15

1 - LC50s correspond to values for stage DEATH, all others are EC50s.

2 - Moribund animals which died during a 24-h post-exposure recovery period.

3 - "Ecologically dead" animals which did not fully recover within a 24-h post-exposure period.

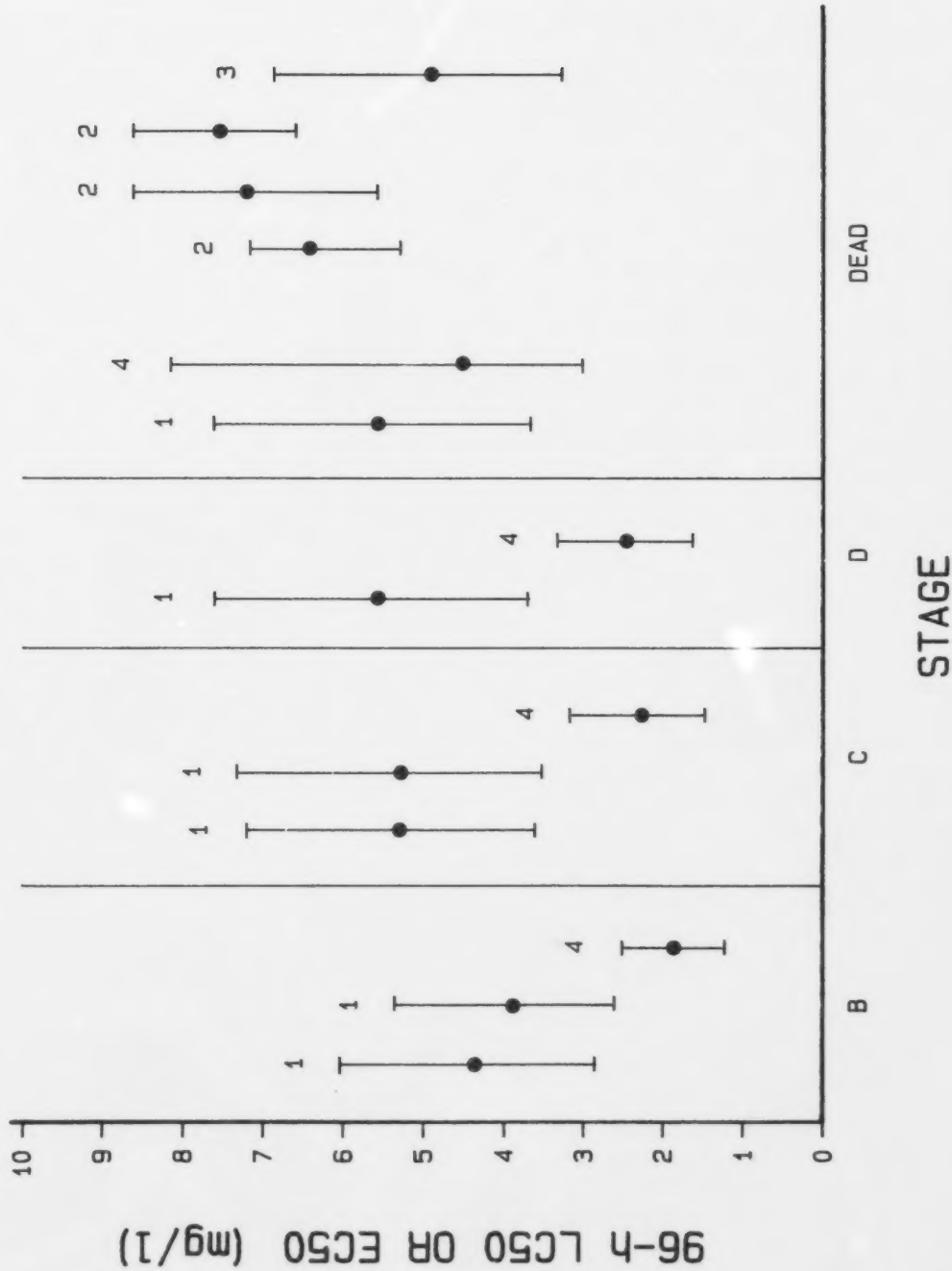


Fig. 3. 96-h LC50s and 96-h EC50s of *M. oculata* exposed to oil-in-water dispersions. Data are grouped by behavioral stage, moribundity, and "ecological death" to show differences between replicate EC50s (or LC50s) obtained using different experimental methods. Vertical lines correspond to 95% confidence limits. Numbers above the lines correspond to the experimental method used: 1 = 750-ml sealed jars; 2 = 1-L open beakers; 3 = 1-L sealed beakers; 4 = 750-ml sealed jars.

Similar trends are shown by the binomial test results. Approximate LC50 and EC50 values ranged from 2 to 9 mg/l and the lowest ones also occurred in method no. 4 (2 - 4 mg/l). EC50s for stages B, MOR24, MOR48, ECO24 and ECO48 were usually 1 - 3 mg/l lower than the 96-h LC50.

Water-soluble fractions. 96-h LC50s for WSF83 and WSF86 ranged from 486 to 624 µg/l. The two mixtures did not produce statistically different results (Fig. 4). For both mixtures, EC50s were the lowest for stage B, and values increased in the following order of stage: ECO24 & 48, MOR24 & 48, C, D and DEATH (Fig. 5). In both cases, EC50s for stage B were statistically lower than the LC50. Also, tests conducted with WSF86 resulted in EC50s for "ecological death" which were statistically lower than the LC50. Results from the binomial test show similar patterns.

Cannibalism and molting. The incidence of cannibalism during 96-h tests was highest in low concentrations of OWD (i.e. 1 - 4 mg/l) and low to intermediate concentrations of WSF (i.e. 259 - 685 µg/l). In most cases, cannibalism occurred because mysids which had lost equilibrium or died (i.e. stages B, C, D and DEATH) were eaten by more resistant individuals (i.e. stage A's). This did not occur at high concentrations because all mysids in test jars lost equilibrium rapidly, including the most resistant ones. Molting occurred in low and intermediate concentrations of toxicant as well as in control jars. There were no detectable relationships between the percent cannibalism or molting and 96-h LC50s. The lowest LC50s, indicating increased sensitivity, were rarely related to the highest incidence of cannibalism and/or molting.

Post-exposure recovery. Table 5 shows the percent delayed mortality and "ecological death" for *M. oculata* during post-exposure periods in clean seawater. Latent effects were consistently higher for organisms exposed to OWDs as opposed to WSFs.

DISCUSSION

The mixing method used in toxicity tests greatly influences the composition of oil-in-water solutions. Vigorous shaking, as used here in the preparation of oil-in-water dispersions, creates a solution resembling the parent oil in composition (NRC 1985). Gentle stirring on the other hand, produces a water-soluble fraction which is enriched in aromatic hydrocarbons (Anderson et al. 1974a). Although similar patterns were found in this study, WSFs prepared by the method of Anderson et al. (1974a) were not saturated with aromatic hydrocarbons. Conversely, OWDs produced by shaking contained a higher proportion of several aromatic compounds from ethylbenzene to C3-naphthalene. These results suggest that short-term vigorous shaking is a more efficient method of dissolving all volatile oil fractions and producing a solution saturated with aromatic hydrocarbons. Gently stirring oil-in-water solutions selectively dissolves a high proportion of soluble fractions (i.e. mono-nuclear aromatics) but a lesser proportion of those which require more mixing energy, such as the di- and tri-nuclear aromatics (Rice et al. 1977; Carls and Korn 1985; NRC 1985). In order to saturate WSF mixtures, certain authors (Higgins et al. 1982; Murray et al. 1984) have used short-term vigorous shaking of 10-50 ml of oil in 1 L of water followed by a 48-h settling period. Such a method may be useful in cold water toxicity testing because more mixing energy is required to transport oil into the aqueous phase at lower temperatures.

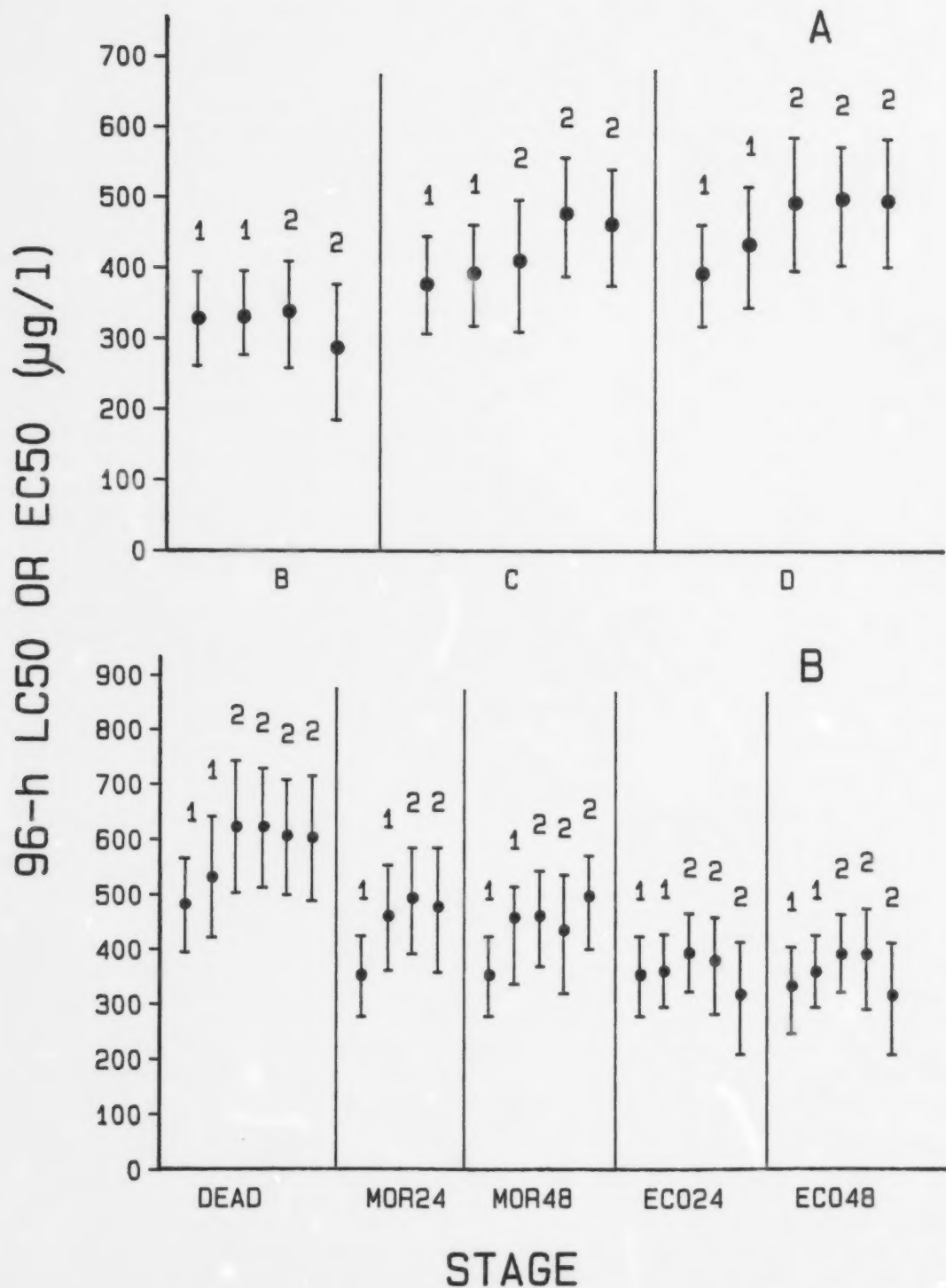


Fig. 4. 96-h LC50s, 96-h EC50s, and confidence limits of *M. oculata* exposed to water-soluble fractions. Data are grouped by behavioral stage (Fig. 4A), moribundity, and ecological death (Fig. 4B) to show differences between LC50s and EC50s due to different WSF mixtures. 1= WSF83; 2= WSF86.

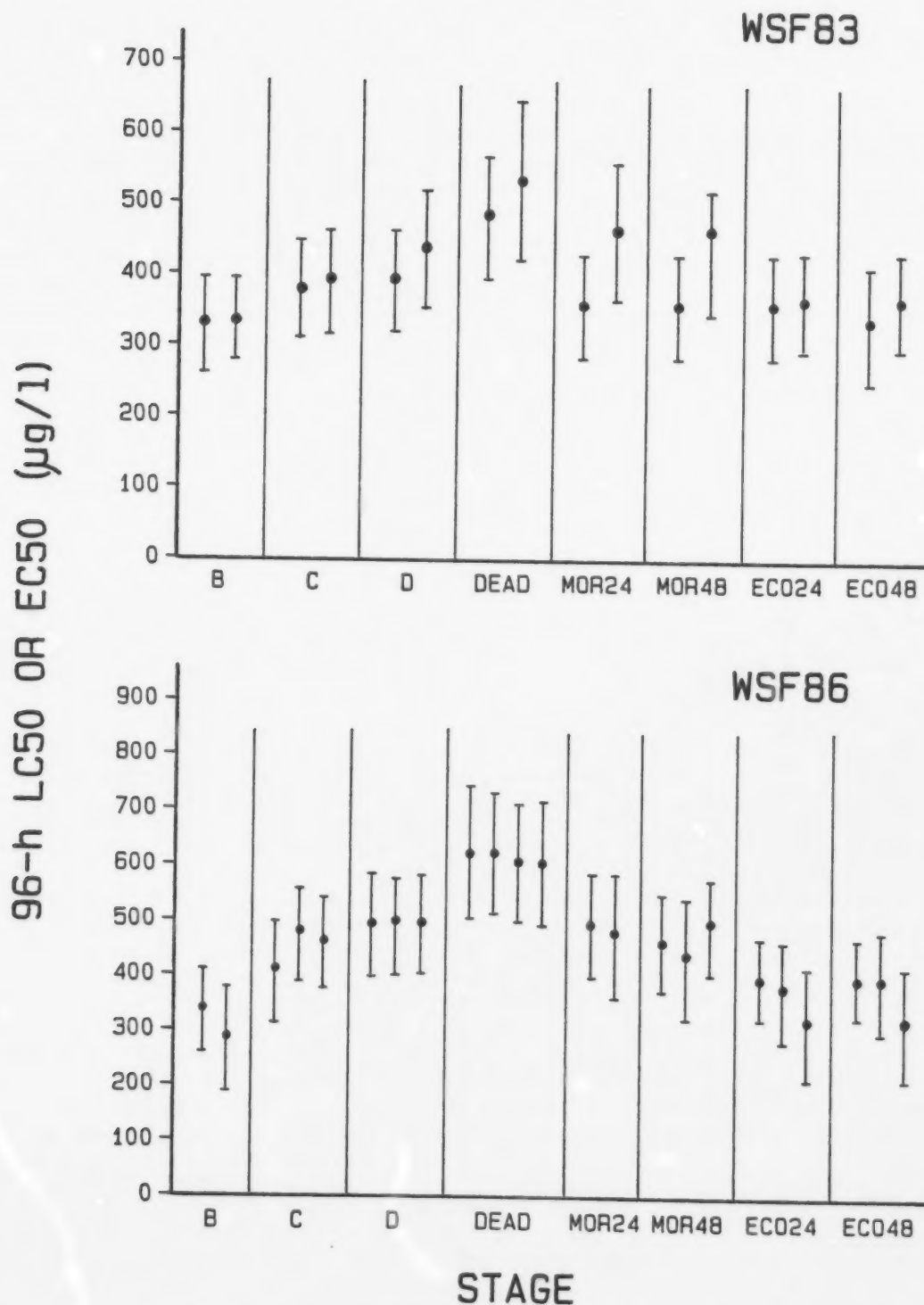


Fig. 5. 96-h LC50s, 96-h EC50s, and confidence limits of *M. oculata* exposed to two different WSF mixtures (i.e. WSF83 and WSF86). The chart shows differences in LC50s and EC50s according to behavioral stage, death, moribundity and "ecological death".

TABLE 5 . Percent delayed mortality and "ecological death" of *M. oculata* during post-exposure to clean seawater.

Toxicant	Method no.	No. of animals transferred to clean seawater	Percent delayed mortality in 24 hrs	Percent delayed mortality in 48 hrs	Percent "ecological death" in 24 hrs	Percent "ecological death" in 48 hrs
OWD43	1	48	12.5	--	29.2	--
	2	83	19.3	38.6	57.8	63.9
	3	50	20.0	42.0	54.0	62.0
	4	26	26.9	34.6	50.0	57.7
WSP43		62	19.4	22.6	30.7	32.3
WSP66		131	15.3	24.4	26.0	26.0

Of the two types of oil-in-water mixtures tested, WSFs were more toxic to young *M. oculata* than OWDs. Although different analytical techniques were used to measure each mixture, comparisons are possible because preliminary analysis of WSFs by fluorescence spectroscopy showed that estimated concentrations were similar to those determined by gas chromatography. Both EC50s and LC50s show that WSFs are at least an order of magnitude more toxic than OWDs. Similar results have been reported for other species of marine fish and crustaceans (Rice et al. 1977). The increased toxicity of WSFs is generally attributed to the higher concentration of aromatic hydrocarbons in solution. The lower toxicity of OWDs is likely due to the fact that a significant portion of hydrocarbons are present as small oil droplets that are less bioavailable than dissolved hydrocarbons (Neff and Anderson 1981). *M. oculata* exposed to OWDs did not experience any apparent adverse physical effects due to oil droplets in solution (e.g. adhesion, ingestion). The oil toxicity is probably a result of chemical toxicity of soluble aromatics, rather than the physical effects of dispersed droplets, as is the case for several other marine species reviewed by Rice et al. (1977). The higher toxicity of dispersions in sealed jars as opposed to open jars further suggests that oil toxicity is due primarily to volatile aromatic compounds. When an approximate 96-h LC50 was calculated using only the concentration of aromatics present in sealed-jar OWD83 (i.e. method no. 4), results showed that the soluble component of the OWD83 was more toxic than that of the WSF83 (i.e. 228 µg/l vs 526-604 µg/l). This increased toxicity may be due to the presence of a higher concentration of alkylated benzenes and naphthalenes which are generally absent in WSFs prepared by gentle stirring. Larger and less-soluble aromatic hydrocarbons are known to be more toxic to aquatic organisms than mono-nuclear aromatics (Anderson et al. 1974b; Neff and Anderson 1981). However, the acute toxicities of several hydrocarbons has also recently been correlated to aqueous solubility rather than chemical structure (Abernethy et al. 1986).

Median lethal concentrations of crude oil-in-seawater mixtures found here for young mysids are among the lowest reported for arctic crustaceans (i.e. 5.5 - 9.2 ppm for OWDs and 0.6 - 0.8 ppm for WSFs). Unfortunately, comparisons between studies are hampered by the lack of experimental standardization. In certain other studies, exposure tests were conducted with open jars and test solutions were aerated, promoting the loss of toxic volatile hydrocarbons. Resulting LC50s may be higher than those determined from sealed-jar tests. In the present study, sealed-jar tests represent a 'worst-case' scenario for *M. oculata* since toxic fractions were retained in test mixtures. This scenario is likely to be comparable to the exposure conditions that could occur in the sea in the vicinity of oil trapped under an ice cover. LC50 values reported here are consistently near the lower limits of lethal concentration ranges for arctic invertebrates and fish (see Percy and Wells 1984). For instance, Foy (1979, 1982) reports 96-h LC50s ranging from 32 to 68 ppm for 6 species of arctic amphipods exposed to OWDs of Prudhoe Bay crude oil. In another study, larval and adult decapods exposed to WSFs of various crude oils had 96-h LC50s ranging from 0.2 to 7.0 ppm (Rice et al. 1976a, 1976b). Although comparisons are difficult to make, *M. oculata* appears to be sensitive to oil-water mixtures, particularly water-soluble fractions. Others have also reported the sensitivity of littoral mysids exposed to petroleum hydrocarbons (Anderson et al. 1974a; Wells 1982; Laughlin and Linden 1983; Smith and Hargreaves 1984; Carls and Korn 1985).

Although median lethal concentrations are useful values for comparing the relative toxicities of oils, or the relative sensitivities of species, they can imply a level of tolerance that is erroneous. In most cases,

ecologically-harmful levels of pollutants are over-estimated (Kimball and Levin 1985; Clark et al. 1986). Hence, any additional information concerning critically-toxic lower levels would enhance the usefulness of an acute toxicity test. In the present study, median effective concentrations causing gross behavioral disturbances, such as loss of equilibrium were determined. These sublethal effects are clearly correlated with concentrations of hydrocarbons in the water and may be useful in predicting the onset of death. In *M. oculata*, acute toxicity followed a pattern of gradual deterioration in activity corresponding to stages B, C and D. In tests with WSFs, only stage B (i.e. loss of equilibrium) occurred at concentrations statistically lower than the LC50. However, in sealed 750-ml jar tests with OWDs, EC50s for stages B, C, D, ECO24, and ECO48 were statistically lower than the LC50. This indicates that the water-soluble component of OWD mixtures was significantly more toxic to *M. oculata* than WSFs. Such a comparison of EC50s and LC50s can yield more useful information concerning acute toxicity than if only LC50s were determined. Post-exposure recovery data also provide a more realistic estimate of acute toxicity (Hansen and Kawatski 1976). EC50s producing "ecological death" show that latent toxic effects in *M. oculata* can occur at concentrations statistically lower than the LC50, although differences do not exceed 3 mg/l. In most cases (i.e. over 90%) stage B animals recovered, but weaker ones (i.e. stages C and D) rarely recovered during a 48-h period in clean seawater (i.e. less than 5%).

Although phenol was used primarily as a reference toxicant, it is also a potentially important marine pollutant. Thus the results of the toxicity tests carried out with this compound are themselves of considerable interest above and beyond their use as a physiological control. Phenols are present in discharge waters from North Sea oil production platforms in concentrations ranging from 2.4 to 7.3 mg/l (Grahl-Nielsen 1987). These compounds may be more hazardous than aromatic hydrocarbons due to their higher water solubility and persistence in the aqueous phase. Acute toxicity tests suggest that prolonged exposure of marine crustaceans to such concentrations may cause lethal or sublethal effects. Tatem et al. (1978) have reported a 96-h LC50 of 5.8 ppm of phenol for grass shrimp (*Palaemonetes pugio*) and the present study shows that *M. oculata* suffers gross behavioral damage during 96-h exposures at 8-10 mg/l.

Lethal and effective concentrations reported in this study clearly show that *M. oculata* is more sensitive to crude oil than many other arctic crustaceans. Furthermore, young-of-the-year mysids are vulnerable to oil exposure because they inhabit areas where hydrocarbons tend to accumulate, i.e. the sub-tidal benthos and under-ice surface. The high sensitivity coupled with the high vulnerability suggests that oil spilled in nearshore arctic waters may have a disastrous effect on *M. oculata* populations. In order to predict more precisely the effects of spilled oil on arctic mysid populations more information is needed about their spatial and temporal distribution, feeding habits and reproductive biology. Physiological and behavioral toxicity experiments are also needed to determine preference/avoidance reactions and chronic effects of low levels of oil on *M. oculata*. This species has been shown to be an ideal subject for toxicity tests due to its sensitivity, its vulnerability, its availability in nearshore waters, and its ease of maintenance under laboratory conditions. *M. oculata* should therefore be considered as a standard test organism for arctic marine toxicity testing and environmental monitoring.

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AVIAN EMBRYO BIOASSAY FOR THE TOXICITY
OF PETROLEUM OILS TO BIRDS

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Petroleum oils are frequently spilled into coastal waters or estuaries near the sea coast, in areas which are extensively used by marine birds for feeding and breeding. Large-scale mortality of seabirds has been associated with many oil spill incidents (Vermeer and Vermeer, 1975; Bourne, 1976). A variety of sublethal toxic effects have been reported in birds following ingestion or external contamination with petroleum oils (Holmes, 1984; Leighton et al., 1985; National Research Council, 1985). Reproductive success of birds can be altered in many ways by petroleum oil exposure (Grau et al., 1977; Cavanaugh et al., 1983; Butler et al., 1988). One well-documented toxic effect of petroleum oils is embryotoxicity (Albers and Szaro, 1978; King and Lefever, 1979; Albers, 1980). Incubating adults, contaminated externally with oil, can transfer enough oil to their eggs to cause embryotoxicity. Laboratory and field studies, using a variety of avian species, have shown that minute quantities of petroleum oil applied to the eggshell can cause mortality of embryos and teratogenicity (Hoffman, 1979b; Macko and King, 1980; Hoffman and Albers, 1984). The mechanism of petroleum oil embryotoxicity is not known. Petroleum oils do not act solely by interfering with the gaseous exchange through the eggshell since up to 50 μ l of propylene glycol or of a paraffin mixture, applied to the eggshell, did not cause embryotoxicity while as little as 5 μ l of Fuel No2 was embryotoxic (Albers, 1977). Petroleum hydrocarbons are transferred from the eggshell to the embryonic tissues (Hoffman and Gay, 1981). The exact compounds responsible for petroleum oil embryotoxicity are not known but the polycyclic aromatic hydrocarbons appear to be the most toxic fraction (Hoffman, 1979a; Hoffman and Gay, 1981; Peakall et al., 1982). Different petroleum oils, with different composition, differ in their embryotoxic potential (Hoffman, 1979a; Hoffman and Albers, 1984). It is not presently possible to predict the potential embryotoxicity of a particular oil on the basis of chemical analysis only. The objectives of this project were to develop an avian embryo bioassay for petroleum oil toxicity and to study the nature of oil-related embryotoxicity.

The Toxicopathology of Prudhoe Bay Crude Oil in Chicken Embryos

Leghorn chicken (*Gallus gallus*) eggs were selected for this study because they are available in large quantity all year long and because the development of the chicken embryo has been studied extensively (Romanoff, 1960). Embryo lethality caused by Prudhoe Bay Crude Oil (PBCO) was evaluated in a 96 hour LD50 test. Pathological changes were studied in surviving embryos to gain insights into the mechanism of embryotoxicity of petroleum oils and to identify possible new endpoints for bioassays of oil toxicity. Treatment was applied on day 9 of incubation, a period of the incubation which is critical with respect to petroleum oil toxicity (Hoffman, 1978). PBCO was applied with a micropipet to the surface of the eggshell just below the airspace and allowed to spread freely (Albers, 1977). Five doses ranging from 1 to 30 μ l PBCO were applied to 5 groups of 35 eggs each. Another group of 35 eggs was used as untreated control. Four days after treatment, percent mortality ranged from 11% in the group treated with

1 ul PBCO to 63 % in the group treated with 30 ul. The LD50 was 14 ul (9-30, 95% fiducial limits). Dose-responsive liver necrosis, subcutaneous edema and enlargement of the spleen and the heart were found in treated embryos. Histological examination revealed extensive zones of necrosis of the hepatocytes at the surface of the liver, cellular casts and mineralization in the renal tubules and accumulation of hematopoietic tissue in the liver and spleen (Couillard and Leighton, 1989b).

Sequential Study of the Pathology of Prudhoe Bay Crude Oil in Chicken Embryos

This study was done to assess the early development and further evolution of lesions in embryos suffering the toxic effects of PBCO. Ten ul of PBCO were applied to the shell of leghorn chicken eggs on day 9 of incubation and morphological changes were studied in embryos surviving 1, 2, 4 and 9 days after treatment. Liver necrosis, renal lesions and subcutaneous edema appeared 2 days after treatment and reached maximal prevalence 4 days after treatment. There was minimal repair of the lesions from day 4 to day 9 after treatment. Thus, the fourth day after treatment is appropriate for examination of the embryos for assessment of toxicity. Pathological changes, including liver necrosis, mineralization in the kidney, infiltration of heterophils in the liver and spleen, subcutaneous edema with formation of large blisters and reduction in the body weight and length were still present on day 18 of incubation, close to hatching time. Lesions found at this late stage of incubation are likely to influence the survival of the chicks after hatching.

Comparative Pathology of Prudhoe Bay Crude Oil and Inert Shell Sealants in Chicken Embryos

This investigation was done to test the hypothesis that the pathological changes observed in PBCO-exposed embryos are due to physical sealing of the shell by the oil. Pathological changes and body weights were compared in 9 day old chicken embryos treated with PBCO, pharmaceutical mineral oil or a sealing film on the eggshell. Embryos exposed to 10 ul or 20 ul PBCO developed marked ascites or subcutaneous edema, extensive liver necrosis, dilation of the heart and cellular casts and mineralization in renal tubules. Wet and dry body weights were normal or above normal in embryos treated with PBCO. No changes were found in embryos exposed to 10 ul mineral oil; embryos exposed to 20 ul mineral oil had slight dilation of the heart. Since 20 ul mineral oil covers approximately the same area of the eggshell as 20 ul PBCO, the lesions observed in PBCO-exposed embryos could not have been due entirely to simple blockage of the pores of the eggshell.

Data from the embryos surviving in eggs wrapped in the sealing film provided further evidence that the toxicity of PBCO to embryos could not be attributed to sealing of the shell. Very few embryos survived in eggs that were wrapped in a sealing film. All the embryos that did survive had greatly reduced body weight compared to control or PBCO-treated embryos. Liver lesions and edema were less severe than in PBCO-treated embryos. Four of these embryos had vacuolation of hepatocytes at the surface of the liver, one had superficial liver necrosis and one embryo had slight ascites. Both the sealing film and PBCO caused lesions that were restricted to the newly formed tissue at the surface of the liver, suggesting that the liver cells that are more sensitive to injury associated with PBCO are also more sensitive to reduced gas exchange and hypoxia (Couillard and Leighton, 1989a).

The Toxicity of Petroleum Oil at Three Different Times of Incubation in Chicken Embryos

These experiments were conducted to establish the optimal age of embryo for use in bioassays for the relative toxicity of different petroleum oils. Microliter amounts of South Louisiana Crude Oil (SLCO) or PBCO were applied to the shell of fertile leghorn chicken eggs on day 8, 8.5 or 9 of incubation. Percent mortality and prevalence of grossly visible lesions were evaluated 96 hours after treatment. The 96-hr LD50s of SLCO at 8, 8.5 and 9 days of incubation were 2.6, 4.3 and 34.3 ul. Five ul PBCO caused nearly 100% mortality in 8 and 8.5 day old embryos while 12 ul caused only 32% mortality in 9 day old embryos. Liver necrosis, edema and increases in body weight and in the ratio of body weight to crown-rump length were found in embryos treated on day 8, 8.5 or 9 of incubation with either SLCO or PBCO. The 9th day of incubation was the most suitable of the 3 incubation times tested for assessment of the toxicity of different petroleum oils. Although the LD50 of SLCO can be measured more accurately at day 8 or 8.5 than at day 9, the extreme sensitivity of the 8 or 8.5 day old embryo would hinder the determination of the LD50 of more toxic oils such as PBCO. Prevalence of liver necrosis in alive embryos can also be determined more precisely with treatment on day 9 of incubation. Growth and fixation of the chorioallantoic membrane to the eggshell are the most important events occurring in the developing embryo from day 8 to day 9 of incubation (Romanoff, 1960; Freeman and Vince, 1974). The 16 fold decrease in sensitivity of the embryo from day 8 to day 9 of incubation suggests that the chorioallantoic membrane is important in the toxic action of petroleum oil.

Bioassays for the Toxicity of Petroleum Oils in Chicken Embryos

The objectives of this study were to determine if petroleum oils, other than PBCO, cause liver necrosis in chicken embryos and to evaluate if liver necrosis can be used as an endpoint for a bioassay of oil toxicity. One ul to 30 ul of six different petroleum oils were applied to the shell of fertile leghorn chicken eggs on day 9 of incubation. Embryo lethality and grossly visible morphological changes were evaluated 4 days after treatment.

LD25s were calculated instead of LD50s because percent mortality was below 50 % in groups treated with 30 ul of the less toxic oils. LD25s were estimated by Probit analysis (Finney, 1971). The slopes of the Probit lines did not differ statistically thus, the LD25s were determined with the assumption that all the lines were parallel. The similarity of the slopes of the dose-responses lines suggest that the six oils have a similar mechanism of toxic action. South Louisiana Crude Oil and Fuel No2 Oil were the least toxic of the oils tested, with LD25s above 8 ul/egg. Arabian Light, Federated, Norman Wells and Prudhoe Bay Crude Oils were more toxic with LD25s ranging from 3.6 to 4.4 ul/egg (Table 1). There is not a good discrimination between the different oils because there is considerable overlap of the fiducial limits of the LD25s.

Liver necrosis and edema were found in embryos exposed to the 6 petroleum oils, further suggesting a common mechanism of toxic action. Prevalence of liver necrosis was determined in embryos surviving 96 hours after treatment and ED25s were estimated by Probit analysis. The ED25 analysis for liver necrosis could discriminate among the toxicities of the 6 petroleum oils slightly better than the LD25 analysis (Table 2). There was a good correlation between the results of the two tests. The ED25 was more reliable and replicable than the LD25 when bioassays were repeated several times on the same oil.

TABLE 1. TOXICITY OF 6 PETROLEUM OILS IN CHICKEN EMBRYOS.
ENDPOINT : MORTALITY.

Oil	LD25 ^a (95% fiducial limits)	Slope
PBCO	3.7 (2.5-5.4)	1.3
FUEL No2	8.5 (5.5-13.1)	1.3
SLCO	14.1 (8.7-23.0)	1.3
ALCO	3.6 (2.1-6.0)	1.3
NWCO	4.4 (2.8-6.8)	1.3
FCO	4.0 (2.4-6.9)	1.3

a : Probit regression lines with reverse estimates of LD25 obtained under the hypothesis of parallelism.

TABLE 2. TOXICITY OF 6 PETROLEUM OILS IN CHICKEN EMBRYOS.
ENDPOINT : LIVER NECROSIS

Oil	ED25 ^a (95% fiducial limits)	Slope
PBCO	3.9 (2.9-5.7)	1.7
FUEL No2	13.1 (8.4-20.5)	1.7
SLCO	18.0 (11.6-28.3)	1.7
ALCO	4.1 (2.7-6.2)	1.7
NWCO	5.0 (3.4-7.4)	1.7
FCO	2.8 (1.8-4.1)	1.7

a : Probit regression lines with reverse estimates of ED25 obtained under the hypothesis of parallelism.

In conclusion, chicken embryos are sensitive to petroleum oil toxicity. Different petroleum oils have different embryotoxicity potential but appear to have a similar mechanism of toxic action as indicated by the similarity in the pathological changes produced in embryos and by the similarity of the slopes of the dose-response curves. Prevalence of liver necrosis in surviving embryos can be used as an endpoint in a bioassay to discriminate among the embryotoxicity of different petroleum oils. Additional studies are needed to further define the mechanism of toxic action of petroleum oils, to correlate the liver necrosis with survival and health status of the chick after hatching and to find which physicochemical characteristics of petroleum oils are associated with embryotoxicity.

ACKNOWLEDGEMENTS

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TANK TESTING OF SKIMMERS WITH WAXY AND VISCOUS OILS

by

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INTRODUCTION

This study involved the testing of several offshore skimmers in a large wave basin to evaluate and compare their effectiveness in recovering spills of conventional and waxy crude oils (and their emulsions) and a viscous residual fuel oil. The additive Elastol was also evaluated for its potential to improve skimmer efficiency.

Study Rationale and Background

Major oil spills off the East Coast of Canada are increasingly likely to involve relatively viscous oils, oils that would pose serious difficulties to currently available spill recovery systems.

The process of evaluating spill countermeasures to deal with waxy and viscous crude oils was begun four years ago by Mobil Oil Canada Ltd. and its partners in their study of Hibernia oils for the Hibernia Environmental Impact Statement (S.L. Ross 1984). Petro-Canada conducted similar studies on the properties of oils from the Terra Nova field (S.L. Ross 1985a). This was followed by two Environmental Studies Research Fund (ESRF) projects: the first was a paper evaluation of the feasibility of countermeasures for spills of waxy, viscous oils (S.L. Ross and Hatfield 1986), and the second was a major laboratory study of the fate and behaviour of waxy crude oil spills (S.L. Ross and DMER 1988). Most recently, a large trial of offshore spill containment and recovery equipment was carried out near St. John's, Newfoundland; the oil used in these tests was selected for its resemblance to the waxy oils recently discovered in the Grand Banks (S.L. Ross 1987).

Although much has been learned about the fate and behaviour of waxy and viscous oil spills and countermeasures for these oils, additional tank testing was required to evaluate the potential application of various skimmers for the recovery of these oils offshore.

EQUIPMENT AND METHODS

Test Tank

The Outdoor Ship Manoeuvring Basin at the Montreal Road campus of the National Research Council of Canada in Ottawa was used for the tests. This tank (Figures 1 and 2) was ideal for the study, being large (120 m x 60 m x 3 m deep) and fitted with a wave generator capable of generating regular waves 0.5 – 0.75 m in height. Facilities at the site included a workshop, control tower, wavemaker, wave beach and flood-lighting for night work.



Figure 1: Test site — NRC Outdoor Ship Manoeuvring Basin and Building M-42



Figure 2: Wave tank (looking towards wave beach)

Although there is no facility for creating currents in the tank, this was not felt to be a disadvantage; in fact, the use of tow bridges to create relative water velocities severely constrains available test times to that required to traverse the tank.

Containment booms were used to thicken the oils to thicknesses representative of offshore recovery operations (5–10 cm). Figure 3 shows the placement of the various booms. The test area was formed by a 36-inch boom in a square configuration 7.5 m on a side containing an area of about 60 m². Subsequently, a home-made silt boom, consisting of two 15 m x 4 m plastic tarpaulins suspended from 18-inch boom was used to line the test area boom. The perimeter of the tank was lined by containment boom to minimize oiling of the tank walls. A 36-inch boom was deployed inside the perimeter boom as a secondary containment system. A sorbent boom was placed across the tank in front of the wave beach to absorb any sheens escaping from the containment booms.

The Skimmers

Four skimmers were tested, the Walosep W-2 (Figure 4), the Framo-ACW 400 (Figure 5), the GT-185 (Figure 6), and the Heavy Oil Skimmer (Figure 7). Detailed specifications of each may be found in the report (S.L. Ross 1989). These four skimmers were selected for the test program for the following reasons. The Walosep, manufactured by Mattssonprodukter of Sweden, was singled out in the ESRF countermeasures study (S.L. Ross and Hatfield 1986) for its potential applicability to waxy oils. The Framo skimmer (manufactured by Frank Mohn of Norway) was of interest because it is the main weapon in the countermeasures arsenals of both industry and Coast Guard on the East Coast. Similarly, the GT-185 (manufactured by Pharos Marine of Sweden) is an important part of the Coast Guard inventory. The prototype Heavy Oil Skimmer was developed by Canpolar and the Coast Guard specifically for viscous bunker oils. The three latter skimmers were involved in the recent field trials offshore St. John's.

The hydraulic arm of the Framo unit was used to deploy and position each of the skimmers within the test area. Both the ACW-400 and Heavy Oil Skimmer heads were powered by the Framo diesel/hydraulic power-pack mounted on the unit. The GT-185 and Walosep W-2 skimmer heads were powered by a GT-185 diesel/hydraulic power-pack. This power-pack (delivering up to 80 l/min @ 50–60 bar) did not produce sufficient hydraulic power for the Walosep W-2 pump (requiring 65 l/min at 170 bar) thus the pump could only be operated at up to 35% of its capacity. Fittings were not available to connect the Walosep W-2 to the Framo diesel/hydraulic power-pack (producing up to 250 l/min @ 250 bar).

Two MI-30 disc skimmers, although not tested, were used to recover oil that escaped the test area.

The Oils

Three oils were used to test each skimmer: IPL Sweet crude oil, a conventional pipeline crude from Alberta (similar in properties to the familiar Alberta Sweet Mixed Blend) served as a benchmark for the testing, a light Bunker C, representative of the viscous, residual fuel oils commonly spilled in Canadian waters; and Terra Nova C-09 crude oil, obtained from a Petro Canada well test on the Grand Banks during the

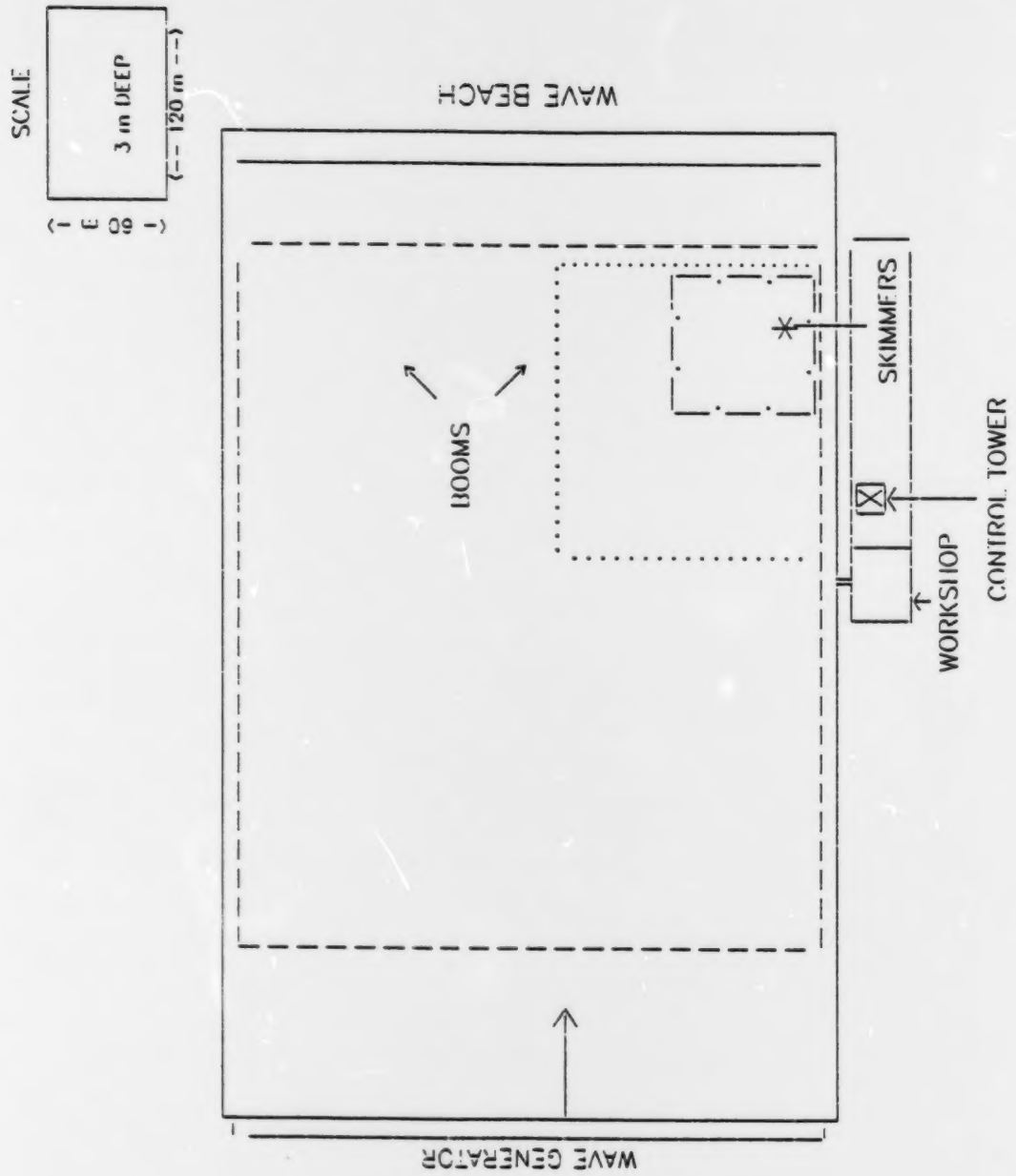


Figure 3: Boom layout in wave tank

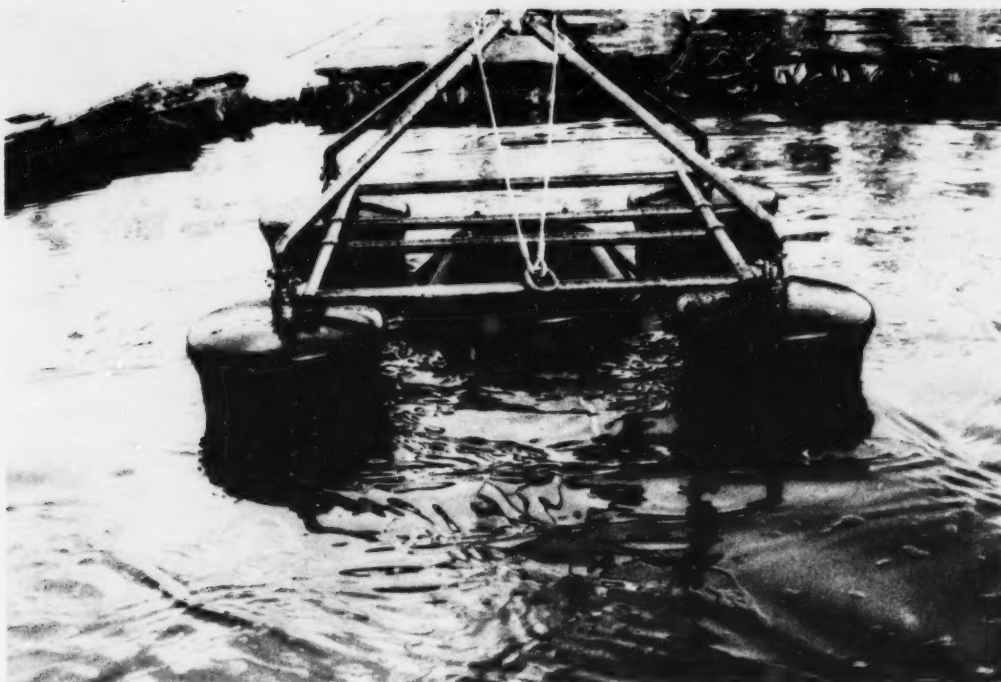


Figure 4: The Walosep W-2 skimmer



Figure 5:
The Framo ACW-400 skimmer head

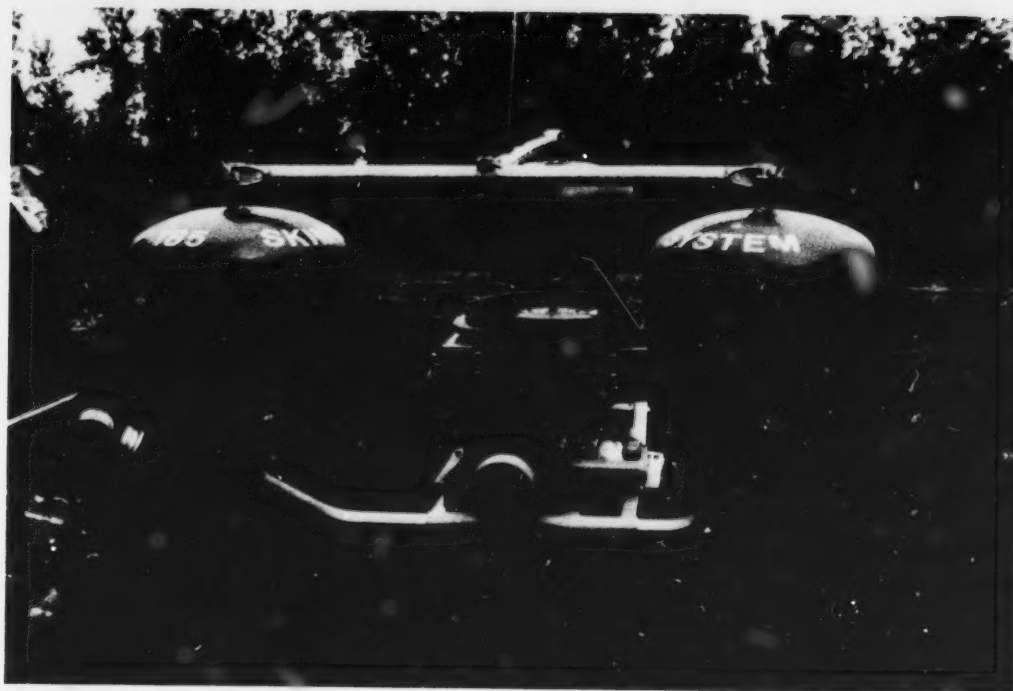


Figure 6: The GT-185 skimmer

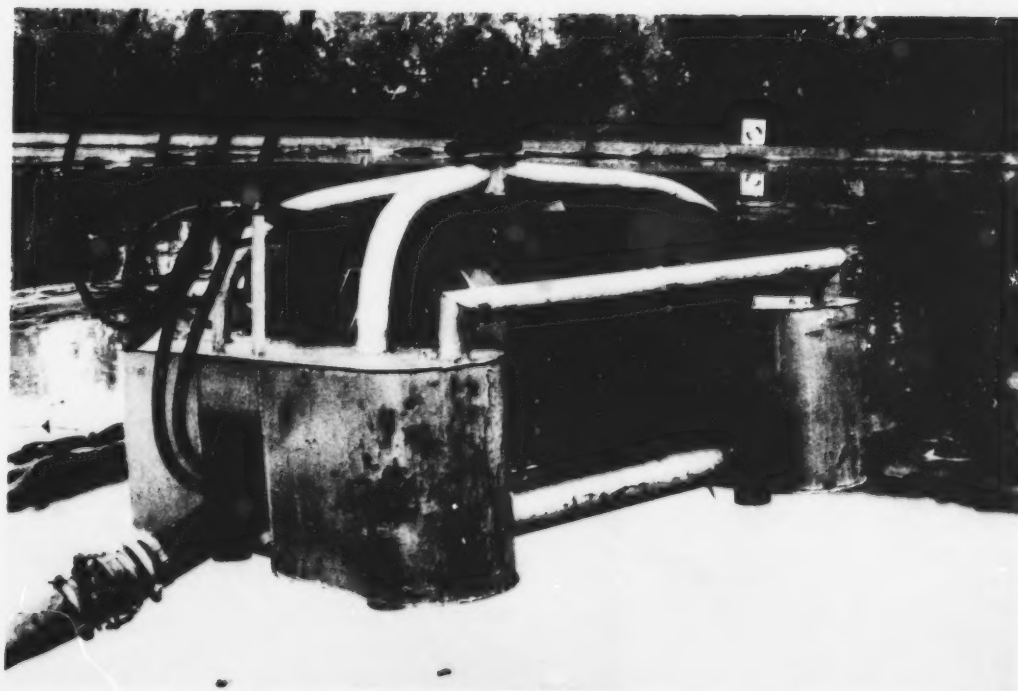


Figure 7: The Heavy Oil Skimmer

summer of 1988. The first two oils were obtained from the Petro Canada refinery in Clarkson, Ontario. Table 1 gives the physical properties of each fresh oil.

TABLE 1
Properties of Test Oils (fresh)

Oil Type	Density @ 15°C (g/ml)	Viscosity @ 15°C cSt*	Pour Point (°C)
IPL Sweet crude	0.844	7.2	<0
Bunker C	0.958	9300	0
Terra Nova C-09 crude	0.834	36	10

* 1 centistoke = 1 mm²/s

The Terra-Nova C-09 crude oil was heated to at least 45°C and circulated for several hours before each transfer on its journey from the rig to Ottawa. This procedure ensured that the waxes remained in solution in the oil and did not remain precipitated on cold tank walls after a transfer. Upon arrival and transfer in Ottawa the oil was kept heated in a steam-traced, insulated tanker.

The Bunker C was reused for each skimmer, weathering and reuse presumed to have little effect on its properties. Conversely, each test with crude oil was started with fresh crude.

Site Layout and Ancillary Equipment

Figure 8 shows a schematic diagram of the test site. The major pieces of ancillary equipment at the tank were: two 23 m³ (5000 gallon), steam-traced portable tanks for dewatering and storage of used crude oil after testing; two 5 m³ polyethylene, steam-traced tanks for dewatering and storage of Bunker C after each test; a 32 m³ two-compartment, steam-traced, insulated tanker for storage of the fresh crude oil; a Cleaver-Brooks Model CBH-100 (980 kW) portable steam boiler to provide steam for tank heating and a steam siphon which was tested for its emulsion-breaking capabilities (Guenette 1989); a portable diesel/electric generator to power the steam boiler; two portable steam cleaners and several Spate 3-B portable pumps. The dewatering/storage tanks were placed in plastic-lined temporary berms to contain any accidental spillage.

Oil for each test was pumped from the tanker (or the 5 m³ tanks in the case of Bunker C) into a manifold and then to a spill plate floating in the test area (Figure 9). This spill plate consisted of a plastic drum with an inflated truck tire attached to its rim for buoyancy and stability in waves. The discharge hose was suspended vertically into the drum with the end about halfway into the drum. This permitted the drum to move up and down with the waves without affecting the discharge hose. Once each test's oil had been pumped the hoses were flushed with water from the basin.

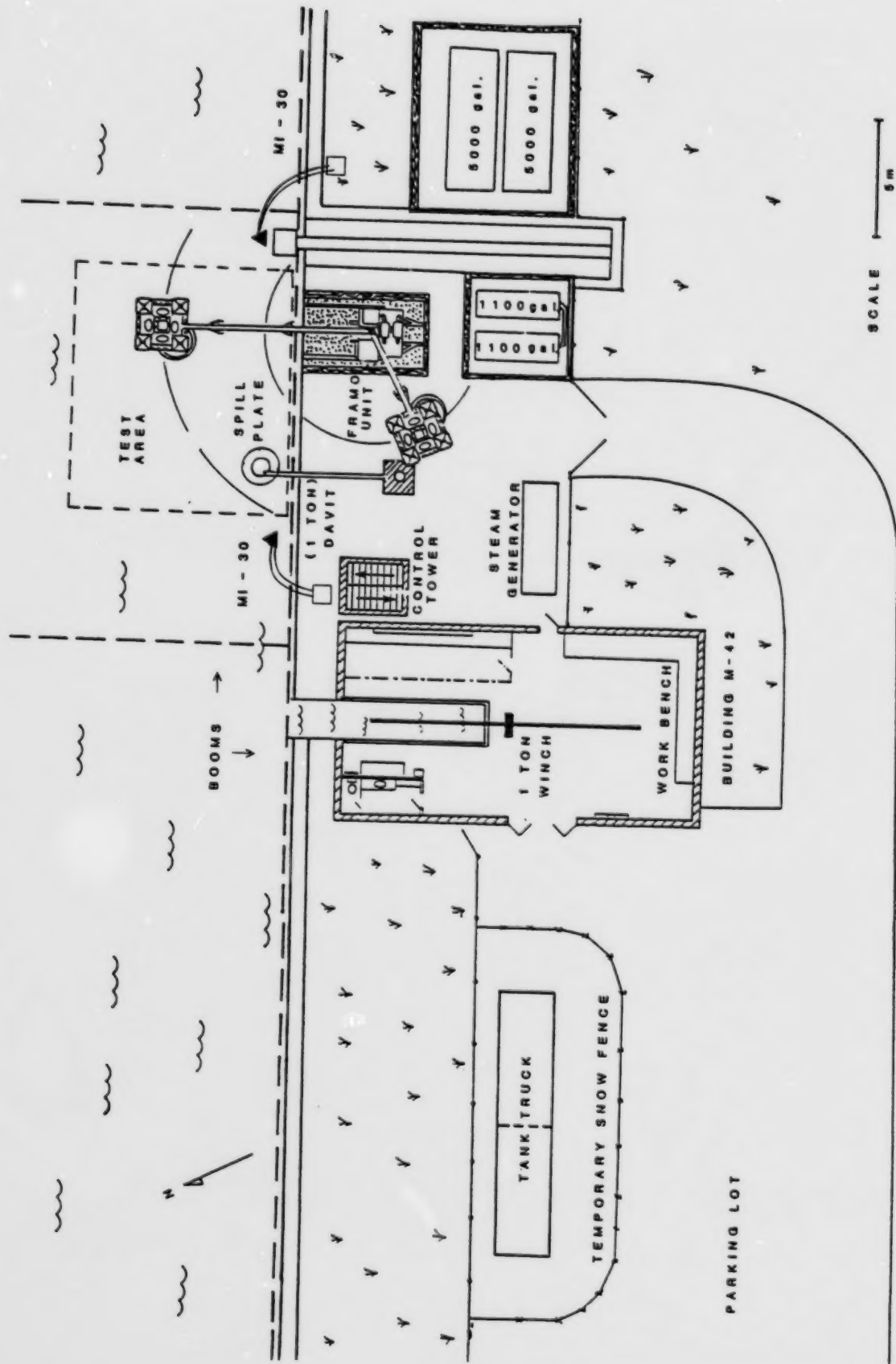


Figure 8: Equipment layout



Figure 9: Spill plate in enclosed test area

Recovered oil from a skimmer test was pumped through a test section of pipe where pressure, temperature and flowrate were measured and samples taken, then through a steam siphon (Guenette 1989), into the manifold and then back to the spill plate. Upon completion of each test the skimmer pump was stopped and the hose from the manifold to the spill plate and the spill plate itself were flushed with water pumped from the basin. The skimmer pump was then restarted and the recovered oil pumped through the test section, steam siphon and manifold to the appropriate holding tank. Low and high pressure water was used to herd the last of the oil to the skimmer; final polishing of the test area and booms was accomplished by MI-30 skimmers and sorbents. Complete details on the analytical equipment and techniques may be found in the report.

Skimmer Testing Procedures

The following steps were undertaken for the test of each skimmer with each oil:

1. A known volume (determined by manually dipping the holding tank) of oil was placed in the test area. This volume was approximately 2.7 m^3 for the tests involving IPL Sweet crude, 3.4 m^3 for the tests involving Terra Nova C-09 crude and 4 m^3 for the Bunker C tests. These volumes equate to initial slick thicknesses of about 5, 6 and 7 cm respectively.
2. The oil was allowed to cool for about an hour to reach ambient temperature. In the case of three of the tests with the Terra Nova crude (the Heavy Oil Skimmer test being the exception) the oil was allowed to cool overnight and gel.
3. The skimmer was placed in the oil and recovery started. The recovered oil was recycled through the test section and manifold to the spill plate. Skimmer variables (i.e., pump rate, weir immersion, disc speed) were varied about every 20 minutes. About 5 minutes after each change (one every 30 minutes if no changes were made) a sample of the recovered fluid was taken for analysis. This procedure was followed for a period of about 2 hours, depending on the skimmer, with no waves in the tank.
4. The waves were then started and the above procedures repeated in waves. The wave height was measured at the tank wall beside the test area using a rule. Wave period was measured by obtaining the time for 10 crests to pass. Wavelength was determined by measuring the distance between successive crests.
5. Following completion of the tests in waves the skimmer was lifted out of the test area and Elastol was applied. This was accomplished by spraying an aqueous slurry of a preweighed amount of Elastol onto the oil in the test area. Mixing and reaction of the Elastol with the oil was accomplished either by continuing the waves during and after addition of the Elastol or by mixing using water pumped from the basin by a fire pump (Figures 10 and 11). For the one test of Elastol on Bunker C the Elastol was applied as a slurry in diesel oil to permit better penetration into the viscous Bunker C.
6. The skimmer was replaced in the tested oil and the test procedures above repeated over a short duration test (about 1 hr) involving measurements both with and without waves if warranted.

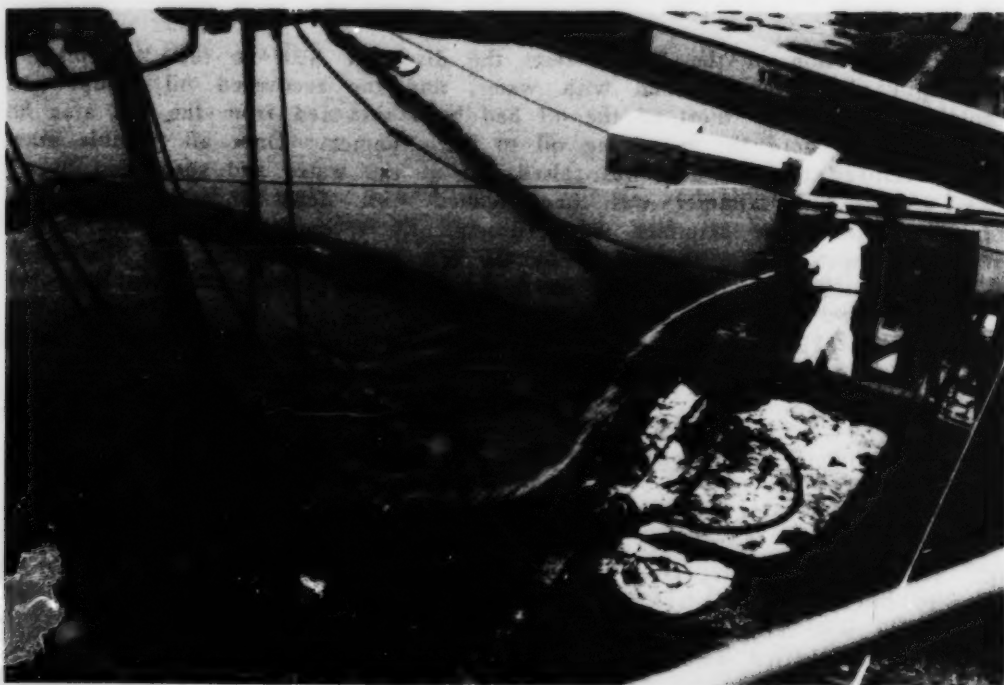


Figure 10: Application of slurried Elastol to oil by hose

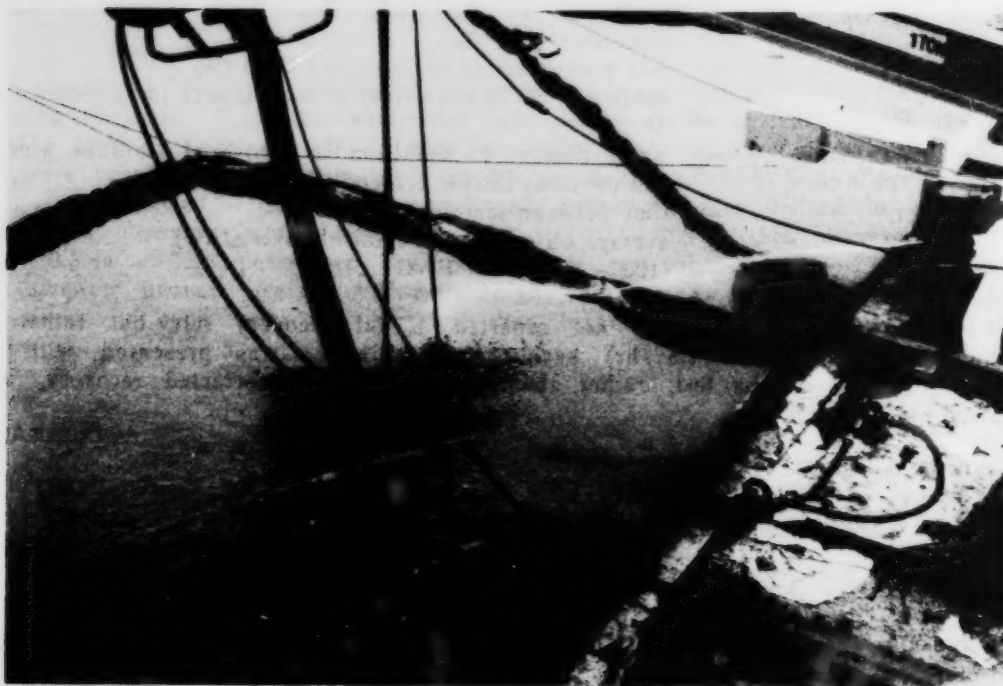


Figure 11: Mixing of Elastol with oil using a fire pump

7. Upon completion of the Elastol tests the discharge hose to the spill plate and the spill plate were flushed with water, and the recovered oil pumped to a holding tank. Once most of the oil had been skimmed from the test area hoses were used to herd the remaining oil to the skimmer. Once all possible oil had been removed the skimmer was raised out of the water and suspended over the test area. The skimmer was then cleaned with steam and hot water. The drippings from the skimmer were subsequently recovered by MI-30 skimmers and/or sorbents. The inner face of the test area booms was also flushed with water to eliminate contamination of the next batch of oil by Elastol-treated oil.
8. The cleaned skimmer was removed from the test site and the next day's skimmer delivered and rigged to the Framo unit ready for its test.

Calculation of Skimmer Performance Data

Three pieces of data were used to calculate performance for each skimmer setting: fluid recovery rate, free water content and emulsion water content. It was necessary to calculate the water entrainment rate of the skimming device because the recovered fluid was recycled back into the test area; this required analyzing the rate of increase of emulsified water in the recovered fluid over time. The equation used to accomplish this was:

$$Q_W = Q_F (FWC/100) + V_{oil} ((EWC_i - EWC_{i-1}) / (AOC \times \Delta t))$$

where	Q_W, Q_F	=	flowrates of entrained water and recovered fluid respectively (m^3/hr)
	FWC	=	free water content of recovered fluid (%)
	V_{oil}	=	volume of oil (water-free) in the test area (m^3)
	EWC_i, EWC_{i-1}	=	water content of emulsion in recovered fluid in present and previous sample respectively (%)
	Δt	=	time between samples (hr)
	AOC	=	average oil content of emulsion over Δt (%)
		=	$(100 - (EWC_i + EWC_{i-1})/2)$

Corrected recovery rates are not reported as oil recovery rate but rather as oil/emulsion recovery rate (m^3/hr) because the skimmer was presented with an emulsion for some of its test, rather than pure oil. The corrected recovery rates were determined by:

$$O/ERR = Q_F - Q_W$$

The oil/emulsion content factor (%) was calculated from:

$$O/ECF = 100 (1 - Q_W/Q_F)$$

Since the skimmers were operated in a static mode, calculation of oil recovered vs. oil presented was not possible.

RESULTS AND DISCUSSION

General

Table 2 shows the initial conditions (oil volume and thickness) for each of the tests. After the cleanup following the first test with Bunker C (with the Framo ACW-400) it was decided that the test schedule would be rearranged and all Bunker C tests performed on consecutive days. The reasons for this were: first, considerable oil was wasted during the cleanup and second, the cleanup required considerable effort. As such, the water content of the Bunker C used for the other skimmers increased steadily.

Due to unusually warm weather in the Ottawa area preceding and during the tests the water temperatures in the tank were not as low as desired. The major effect of this was that the Terra Nova C-09 crude, when fresh, was not at a temperature below its pour point. In order to attempt to overcome this problem the Terra Nova C-09 crude was placed in the test area the night before the tests of the Walosep W-2, GT-185 and Framo-ACW-400 skimmers. This allowed the oil to weather somewhat and cool to the lower night air temperatures. In the morning, the oil on the surface of the slick would have gelled (Figure 12). After about 30 minutes of testing, however, the bottom portion of the slick (in contact with the warmer water) would have mixed through the test area and the waxy oil would refluidize. Sunlight on the test slick seemed to accelerate the process. It was decided not to delay the Terra Nova C-09 crude tests until the water cooled further because of the considerable expense involved in waiting and the number of personnel and equipment at the site from St. John's.

Figure 13 shows the variation in wave height measured at the test area as a function of time. Once the wavemaker was started at the selected setting the waves quickly built up to about 0.3 - 0.4 m in height. At the selected wavemaker setting the wave beach could not completely absorb the generated wave and a portion of the wave was reflected. As the generated and reflected waves drifted in and out of phase, the measured wave height increased to 0.7 - 0.8 m then decreased to about 0.4 - 0.5 m. The period of this phase drift was about 1.5 - 2 hours. This phenomenon proved useful as wave height became an unintentional, additional parameter in each test, providing further information on the abilities of each skimmer.

Skimmer Tests

The following is a summary of the tests performed with the four skimmers; detailed descriptions may be found in the report (S.L.Ross 1989).

TABLE 2

Initial Test Conditions

Skimmer Type

OIL TYPE	ACW-400	GT-185	WALOSEP W-2	H.O.S
IPL Sweet	<u>2.7</u> 47 17	<u>2.7</u> 47 18	<u>2.6</u> 45 15	<u>2.6</u> 45 18
Bunker C	<u>4.0</u> 69 18	<u>2.5 (5.0)</u> 43 (87) 18	<u>2.5 (6.0)</u> 43 (115) 14	<u>2.5 (7.8)</u> 43 (137) 17
Terra Nova C-09	<u>3.4</u> 59 13	<u>3.3</u> 57 12	<u>3.3</u> 57 15	<u>3.5</u> 61 15

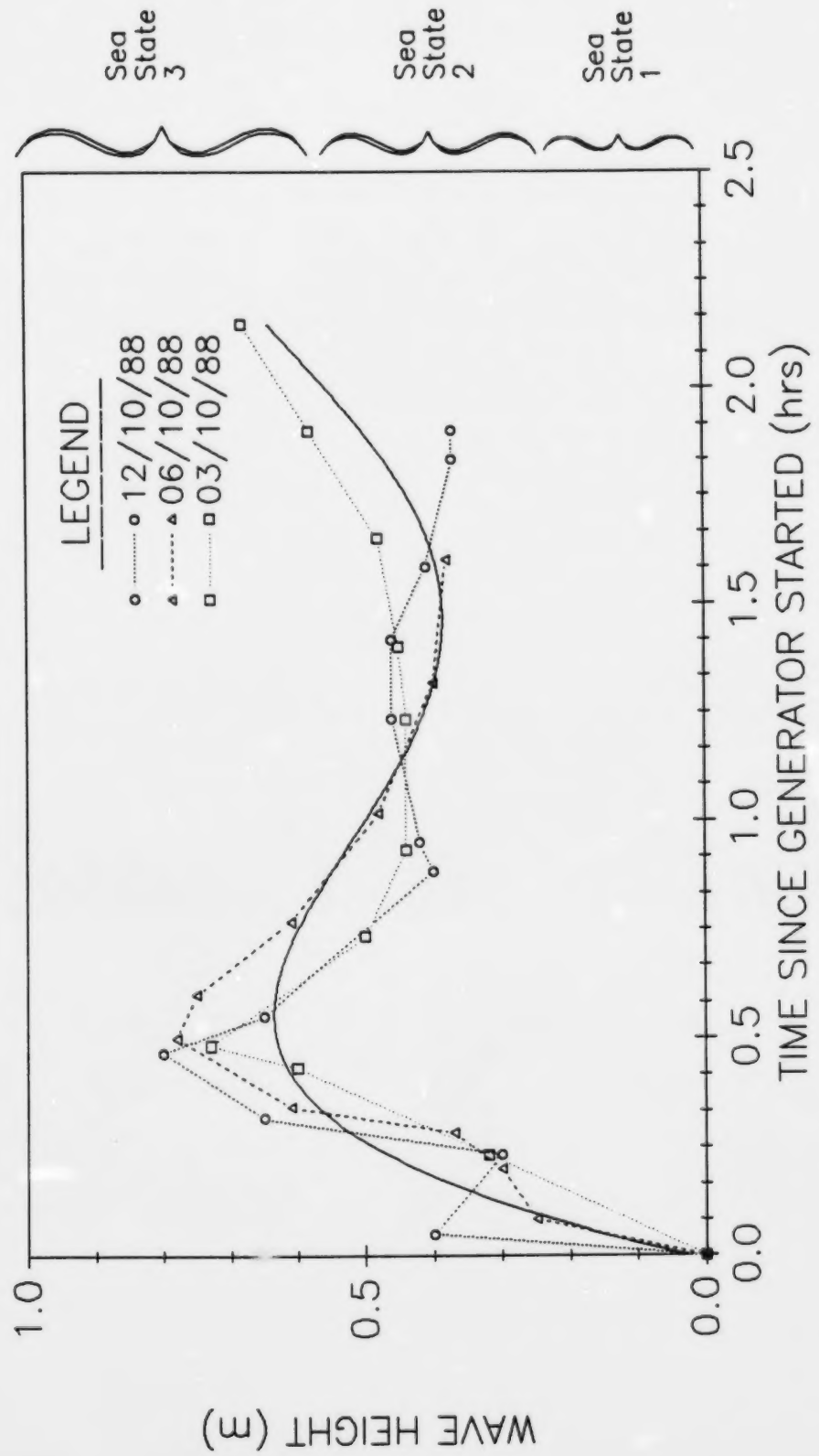
Legend

	INITIAL OIL VOLUME (m ³)	(INITIAL EMULSION VOLUME (m ³))
WATER TEMPERATURE (°C)	INITIAL SLICK THICKNESS (mm)	(INITIAL EMULSION THICKNESS (mm))



Figure 12: Terra Nova C-09 test slick gelled after overnight exposure

FIGURE 13
VARIATION IN WAVE HEIGHT WITH TIME



Framo ACW-400

Figure 14 shows the steady-state oil/emulsion recovery rates (O/ERR) measured for the Framo ACW-400 skimmer as a function of recovered fluid viscosities. The recovery rates have been corrected for water entrainment. The general trend of all the data points was an increase in recovery rate with increasing viscosity for oils or emulsions with viscosities up to several hundred centistokes; recovery rates decreased dramatically as the viscosity of the fluid increased above 1000 centistokes. For oils with viscosities less than several hundred centistokes, increasing disc speed increased recovery rate (by about $10 \text{ m}^3/\text{hr}$ for 10 to 15 rpm and an additional $2\text{--}3 \text{ m}^3/\text{hr}$ for 15 to 17 rpm). Comparison of the data for the IPL Sweet tests with that for the Terra Nova tests shows that, for equivalent viscosities, the Terra Nova was recovered at a rate 30–40% lower than the IPL Sweet at both the 10 and 14 rpm disc speeds. Water entrainment was also about 3 times greater for the Terra Nova tests ($3 \text{ m}^3/\text{hr}$) than for the IPL Sweet tests ($1 \text{ m}^3/\text{hr}$).

Oil/emulsion content factors in calm conditions for the Framo ACW-400 ranged from 80% to 97% with IPL Sweet at a disc speed of 17 and 10 rpm; from 75% to 88% with Bunker C and from 88% to 93% with Terra Nova at disc speeds of 17 and 10 rpm. In waves, the oil/emulsion content factor decreased considerably.

In general the Framo ACW-400 skimmer and unit performed reliably throughout the trials and recovered lower viscosity oil and emulsion effectively in calm conditions; however, its propensity to strongly emulsify oil and water entering the pump and the fact that it tended to push oil away from itself in waves exceeding 0.5 m with a 4 s period (Figure 15), detracted from its overall performance. This latter problem could perhaps be overcome by modifying the skimmer head and associated hoses to permit the device to float freely, independent of the hydraulic arm.

GT-185

Figure 16 shows the effect of fluid viscosity and waves on the oil/emulsion recovery rate (corrected for water entrainment) of the GT-185 skimmer. The device performed admirably, showing very little sensitivity to oil viscosity up to about 12,000 cSt. The oil/emulsion recovery rate decreased dramatically at viscosities in the 100,000 cSt range. Although not reflected in the recovery rate results, visual observations indicate that, with a completely gelled waxy oil, the skimmer's performance would be much poorer than reported here, likely in the range of the results at 100,000 cSt viscosity.

Oil content factors were consistently in the 90+% range for the crude oils in both calm conditions and waves. Addition of Elastol reduced these factors to the 50 – 80% range. In the test with Bunker C the oil content factor was 75 – 83% in calm conditions and 8% in waves; removal of the Light Oil Adapter (LOA) may have been responsible for a drop in oil content factor to 20 – 50% in calm conditions.

Removal of the LOA (Figure 17), though recommended by the manufacturer for oils with viscosities over 15,000 cSt, is not recommended for skimming operations in waves; the presence of the bellows-like adapter improves the wave-following of the weir and thus reduces water entrainment.

FIGURE 14
RECOVERY RATE vs VISCOSITY
FRAMO ACW-400

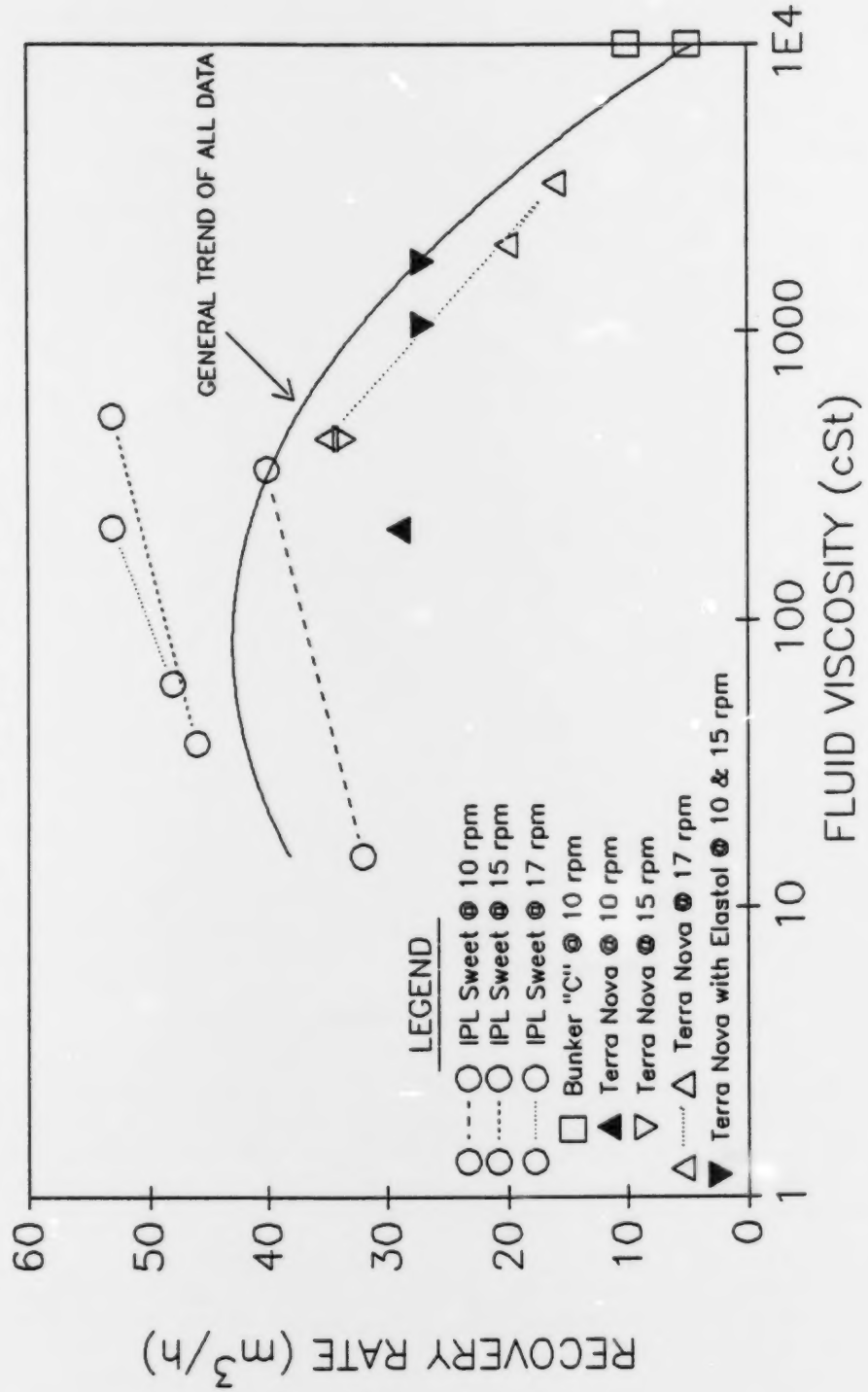




Figure 15: Framo ACW-400 skimmer pushing oil away from discs in waves

FIGURE 16
RECOVERY RATE vs VISCOSITY
GT - 185

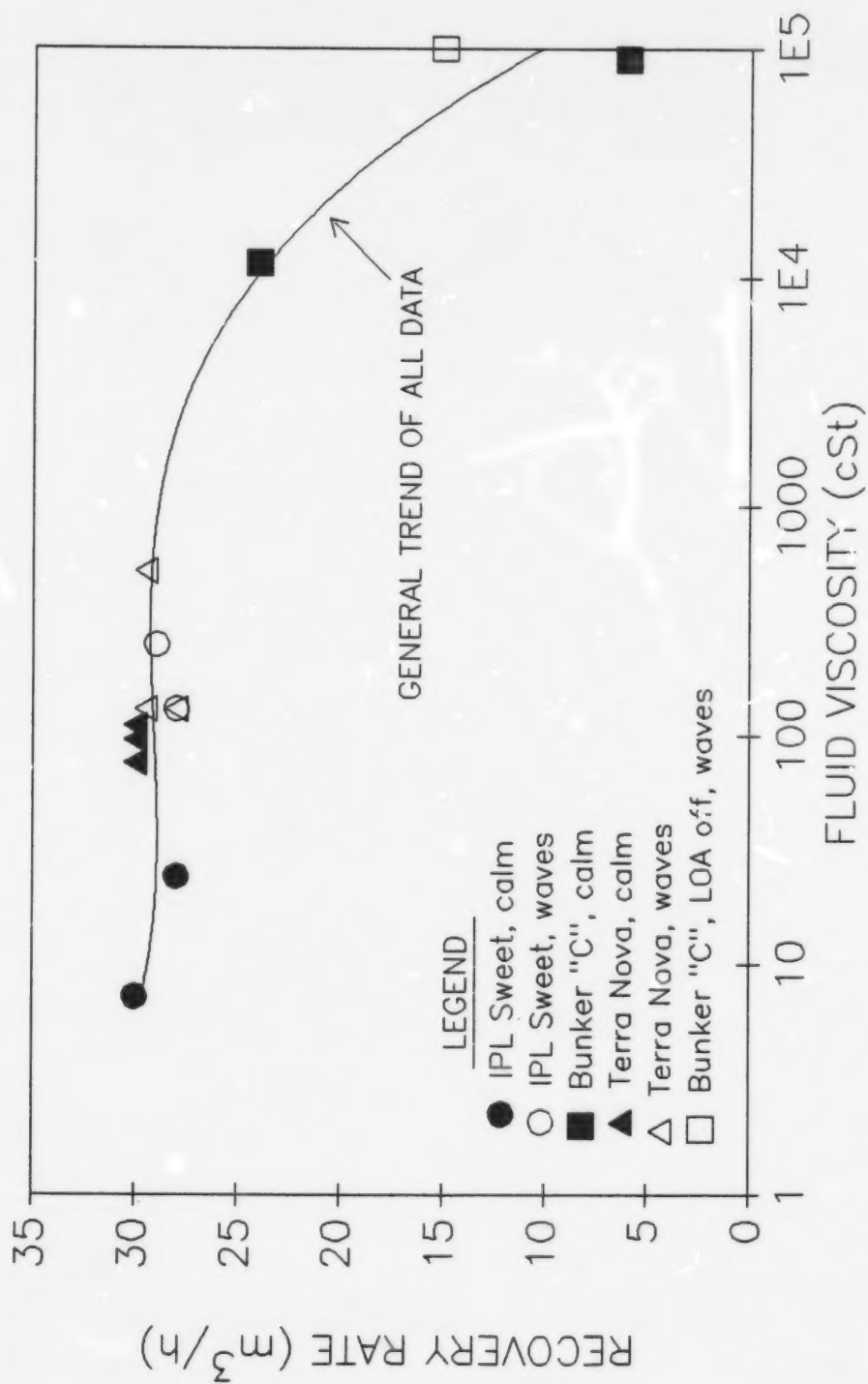




Figure 17: GT-185 with light oil adapter removed

In general the skimmer proved reliable and sturdy, and followed the waves well. Consideration should be given to improving the weir adjustment lever on the power-pack to allow more precise control of the weir position.

Heavy Oil Skimmer

In general, the Heavy Oil Skimmer performed poorly in the tests (Figure 18), proving unable to recover any of the test oils unless Elastol had been added to increase their adherence to the drum material and their cohesiveness.

It is worthy of note that the drums, when rotated in the downward mode, drew in a considerable thickness of the viscous oils beneath the skimmer; modifications to the device could be made to take advantage of this phenomenon in improving the skimmer's performance.

In waves, the skimmer proved stable and followed the waves well; operating the device in the free-floating mode, rather than hard-mounted to the Framo hydraulic arm, was a definite advantage. During operation of the skimmer, it was noted that the scraper blade abraded the absorbent material on the drums. Mounting the scrapers with a spring-loaded adjusting system would allow the scraper to accommodate the out-of-round portions of the drums better than the double-nut system presently used.

Walosep W-2

Figure 19 shows the oil/emulsion recovery rate (corrected for water entrainment) of the Walosep W-2 as a function of viscosity. The general trend was that, in the range up to several hundred cSt, the recovery rate was not a function of viscosity. As the viscosity increased to 100,000 cSt the recovery rate declined to 2 - 5 m³/hr. It must be remembered that this data represents the recovery rate of the skimmer with the pump set at a maximum of only 3½ on a scale of 10. The most impressive feature of the Walosep W-2 was its ability to collect pure, unemulsified oil due to the combined action of the rotor and the pump location. Throughout the tests, even in waves up to 0.7 m, the device entrained virtually no water when skimming crude oil (oil content factors were consistently in the 98+% range); only when operating in very viscous Bunker C did the device collect water (oil content factors ranged from 17 to 47%). Another advantageous feature of this skimmer was its ability to draw in discrete chunks of viscous, gelled oil by the action of the rotor (Figure 20).

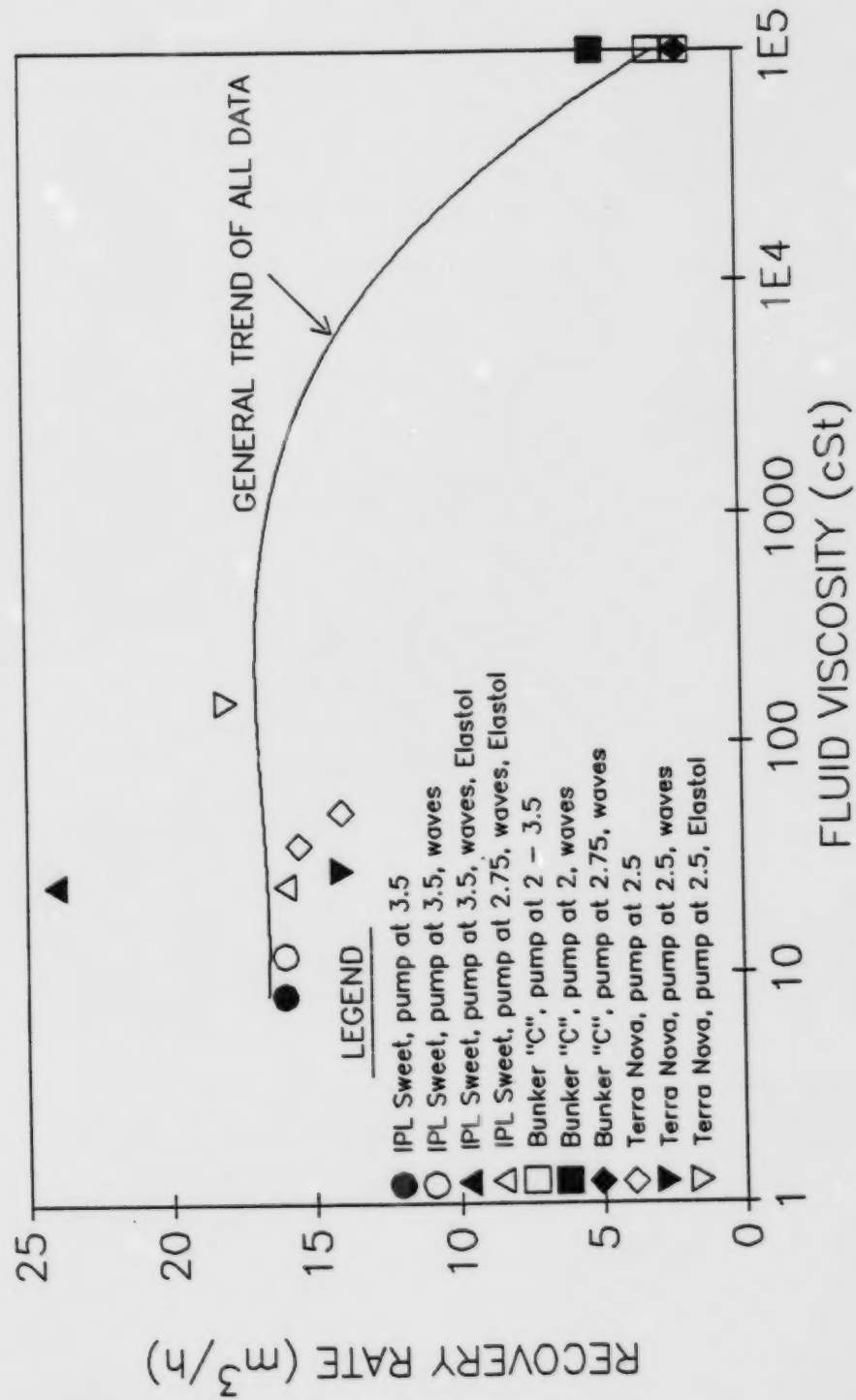
The skimmer operated without difficulty during its test series, though it was underpowered by the GT-185 power-pack. The device followed the waves very well. One minor disadvantage of the device was the need to manually set the weir height, although this was only necessary during its initial deployment.

Application of Elastol to the test crude oils did improve the Walosep W-2's recovery performance by 15 to 40%, although the increased viscosity of the oil caused the underpowered pump to labour, necessitating reductions in pump speed and throughput.



Figure 18: Heavy oil skimmer operating in Bunker C in upward rotation mode

FIGURE 19
RECOVERY RATE vs VISCOSITY
WALOSEP W-2



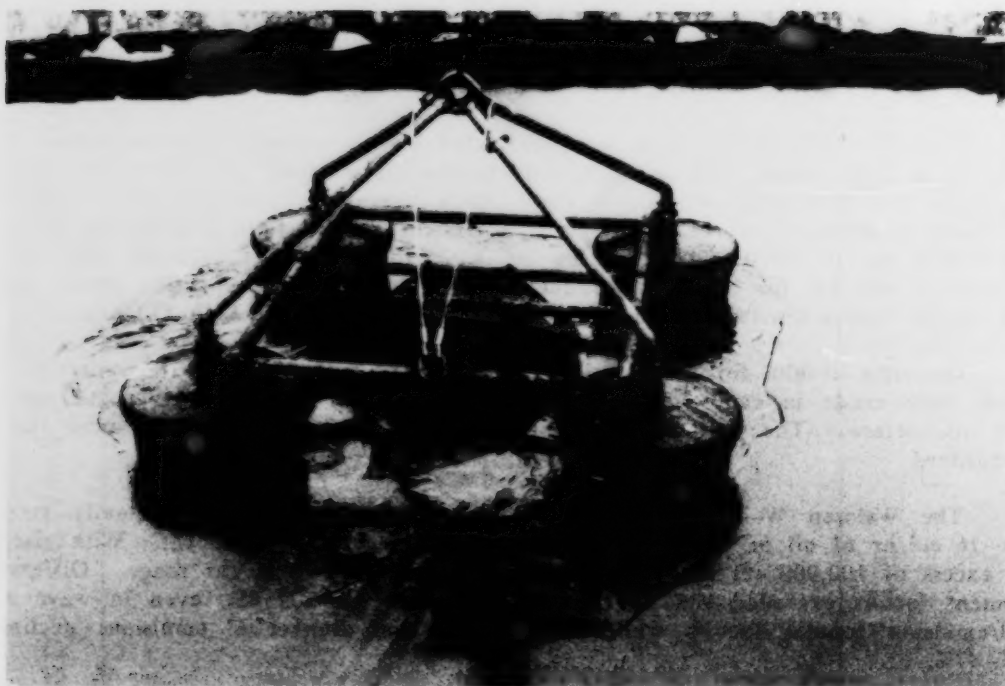


Figure 20: Walosep W-2 in Terra Nova C-09 crude oil

Comparison of Skimmers

Figure 21 shows a comparison of the general trend in oil/emulsion recovery rate as a function of viscosity for the Framo ACW-400, GT-185 and Walosep W-2 skimmers. Table 3 gives the best test results obtained with each skimmer for each oil.

The Framo ACW-400 had the highest measured oil/emulsion recovery rates ($35\text{--}45\text{ m}^3/\text{hr}$) for oils or emulsions with viscosities less than about 1000 cSt. Oil/emulsion content factors varied from 88 to 97% in this range. With oil viscosities in the 10,000 cSt range, oil/emulsion recovery rates fell to $5\text{--}10\text{ m}^3/\text{hr}$ with oil/emulsion content factors in the 75 to 88% range.

Optimum results for oil/emulsion recovery rate with the Framo ACW-400 were $53\text{ m}^3/\text{hr}$ of IPL Sweet crude in calm conditions at a disc speed of 17 rpm and the weir set 5 cm below the oil surface; optimum results for oil/emulsion content factor were 98% with IPL Sweet crude in calm conditions with the weir fully raised and a disc speed of 15 rpm. The action of the skimmer head in waves of 0.4–0.5 m and greater with 4 s periods seriously impaired the device's capabilities.

The GT-185's performance was unaffected by oil viscosity or wave action (in the 0.4–0.6 m high range with a 4s period) recovering a steady $25\text{--}30\text{ m}^3/\text{hr}$ of oil or emulsion over the range 10–10,000 cSt. At a viscosity of 100,000 cSt recovery rates declined to about $10\text{ m}^3/\text{hr}$. Oil/emulsion content factors were consistently 90+% with viscosities up to 1000 cSt, declining to 83% for Bunker C (10,000 cSt) in calm conditions and 8% for emulsified Bunker C (100,000 cSt). Wave action greatly reduced oil content factors when skimming Bunker C, as did removal of the Light Oil Adapter.

Optimum results for oil/emulsion recovery rate with the GT-185 were $30\text{ m}^3/\text{hr}$ with fresh crude in calm conditions and the Light Oil Adapter weir set 2 cm below the oil surface. The optimum oil content factor was 99+%, obtained under the same conditions.

The Walosep W-2 skimmer, despite being underpowered, consistently recovered $14\text{--}16\text{ m}^3/\text{hr}$ of oil or emulsion over a viscosity range of 10–200 cSt. With viscosities in excess of 100,000 cSt recovery rates declined to the $2\text{--}5\text{ m}^3/\text{hr}$ range. Oil/emulsion content factors exceeded 98% in the viscosity range 10–200 cSt, even in wave action; oil/emulsion content factors while skimming viscous Bunker C emulsions declined to 17–47%.

Optimum oil/emulsion recovery rates ($16\text{ m}^3/\text{hr}$) were obtained with the Walosep W-2 with fresh IPL Sweet crude in both calm conditions and waves. Optimum oil/emulsion content factors (99+%) were obtained under the same conditions.

The Heavy Oil Skimmer operated poorly without treatment of the oil with Elastol.

Effects of Waxy Oil

Because of the unusually warm temperatures prior to and during the tests, the water temperature in the basin never fell below the pour point (10°C) of the waxy Terra Nova C-09 crude oil, therefore a full evaluation of each skimmer's capabilities to deal with spills of waxy oils was not possible. Despite this setback, it was

FIGURE 21

RECOVERY RATE COMPARISON

Framo ACW-400, GT-185 and Walosep W-2

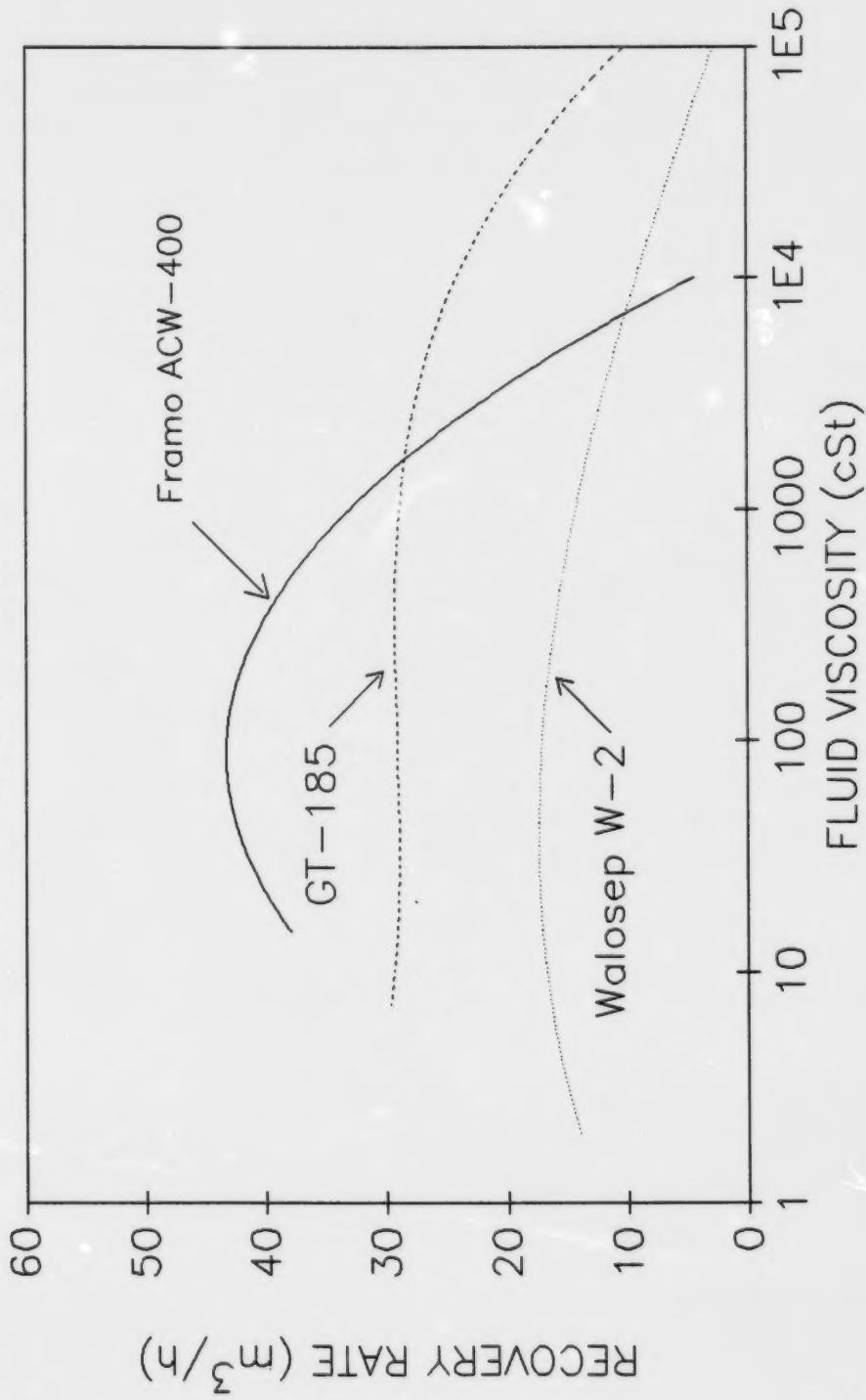


TABLE 3

BEST TEST RESULTS

<u>Skimmer</u>	<u>IPL</u>	<u>Terra Nova</u>	<u>Bunker C</u>	
	<u>Sweet Crude</u>	<u>C-09 Crude</u>	<u>10,000 cSt</u>	<u>100,000 cSt</u>
FRAMO ACW-400				
Corrected Recovery				
Rate	53 m ³ /hr	53 m ³ /hr	10 m ³ /hr	-----
Percent oil/emulsion				
in recovered fluid	98%	93%	88%	-----
GT-185				
Corrected Recovery				
Rate	30 m ³ /hr	30 m ³ /hr	24 m ³ /hr	15 m ³ /hr
Percent oil/emulsion				
in recovered fluid	99+%	99+%	99+%	50%
WALOSEP W-2				
Corrected Recovery				
Rate	16 m ³ /hr	15 m ³ /hr	-----	5 m ³ /hr
Percent oil/emulsion				
in recovered fluid	99+%	99+%	-----	47%
HEAVY OIL SKIMMER				
Corrected Recovery				
Rate	0 (12 m ³ /hr)+	2 m ³ /hr (15 m ³ /hr)+	-----	0 (5 m ³ /hr)+
Percent oil/emulsion				
in recovered fluid	-- (99+%)+	99+% (99+%)+	-----	---

+ with addition of Elastol

possible to draw some conclusions about mechanical recovery of spills of waxy crude oils on the Grand Banks.

The temperatures of the basin during the tests of the Framo ACW-400, GT-185 and Walosep W-2 (12–15°C) did approximate summer water temperatures on the Grand Banks (11.6°C in August – S.L. Ross 1984); the gelled surface oil's behaviour at the start of each test gave an indication of the ability of each skimmer to deal with and process gelled oil forms.

Comparison of the results with the Framo ACW-400 skimming IPL Sweet crude and Terra Nova C-09 crude showed that the recovery rate for the waxy oil (even at 3°C above its pour point) was 30–40% less than for the conventional crude (30 vs. 40 m³/hr at 10 rpm and 33 vs. 53 m³/hr at 15 rpm). Water entrainment rates while skimming waxy oil were three times those while skimming conventional crudes (3 m³/hr vs. 1 m³/hr), resulting in lower oil content factors (88 to 93% vs. 88 to 97%). Had the temperatures been significantly lower, the Framo's performance would likely have been significantly poorer, perhaps even poorer than its performance with Bunker C.

Comparison of the test results with the GT-185 skimming Terra Nova C-09 (at 12°C) and IPL Sweet crude showed little difference in oil/emulsion recovery rates, although during the initial stages of the test with Terra Nova recovery rates were reduced 15% over those recorded later (although this could be attributed to different pump settings) and the oil content factor was 90% compared to 99+% later.

Visual observations of the early action of gelled oil on the surface of the test area indicate that, had the Terra Nova C-09 crude oil been colder, the GT-185 would have had difficulty recovering the semi-solid chunks of oil.

Comparison of the data obtained with the Walosep W-2 operating in Terra Nova C-09 crude oil at 15°C and in the IPL Sweet crude shows no significant difference in oil/emulsion recovery rate (about 15 m³/hr) or oil/emulsion content factor (98+%).

It is worthy of note that this skimmer drew in the chunks of gelled surface waxy oil at the start of its test with Terra Nova crude and also drew in discrete chunks of heavily emulsified Bunker C at the end of that test. The chunks of Bunker C were recovered at a rate of 2 m³/hr with an oil content factor of 10% in 0.68 m waves. This may represent the upper limit of this device to collect waxy oils at temperatures well below their pour point.

In general, the semi-solid nature of gelled, waxy Terra Nova C-09 crude initially on the surface of the test slick impaired flow of that oil into all of the skimmers; the low-adhesive nature of the waxy oil reduced its recovery rate on the oleophilic discs of the Framo ACW-400 skimmer. All three skimmers successfully tested could be applied to recover spills of waxy crudes in summer water temperatures on the Grand Banks; of the three the Walosep W-2 and the GT-185 are better suited to this task than the Framo ACW-400; primarily because of their superior wave response, lower water entrainment rates and gentler pump action. The Walosep W-2 may be best suited in the recovery of gelled oil forms because of the action of its rotor in drawing in semi-solid chunks of oil.

Effects of Elastol Treatment

The most dramatic effect of Elastol treatment of a test slick on a skimmer's performance was for the tests with the Heavy Oil Skimmer. Recovery rates increased from 0 to 12 m³/hr in IPL Sweet crude, from 0 to 5 m³/hr in Bunker C and from 1 to 15 m³/hr in Terra Nova C-09 crude oil with Elastol addition.

Elastol treatment improved the performance of the Walosep W-2 in IPL Sweet crude initially by about 40% (from 16 to 24 m³/hr) but the increased load on the pump necessitated reducing its rate to 16 m³/hr. Elastol treatment of Terra Nova C-09 crude is credited with enhancing the Walosep W-2's recovery rate by about 15% (from 14 to 16 m³/hr).

The addition of Elastol to Terra Nova C-09 crude during the test of the Framo ACW-400 had no measurable effect on recovery rates and increased water entrainment rates. Elastol treatment of the IPL Sweet and Terra Nova C-09 crudes during the tests of the GT-185 skimmer reduced oil/emulsion recovery rates by 25-35% and increased water entrainment rates.

It is worthy of note that, when cleaning up the oil outside the test area, Elastol treatment of the thin (1 mm) slicks of oil visually enhanced the recovery rate of the MI-30 skimmers and allowed oil to be drawn to the skimmers from a considerable distance.

The application of Elastol to the test slicks proved to have negative consequences on the subsequent cleanup of equipment and storage tanks. The Elastol-treated oils and emulsions proved extremely adhesive and difficult to remove from skimmers requiring the use of large amounts of time and high pressure hot water and steam, whereas untreated oil or emulsion could be washed off relatively easily with low pressure cold water. In fact, it proved easier to clean Bunker C off equipment than Elastol-treated oil. Hoses through which Elastol-treated oil had been pumped proved extremely difficult to clean, requiring repeated soaking in diesel fuel followed by flushing with high pressure hot water and steam.

Perhaps the most difficult problem was pumping of Elastol treated oil from the holding tanks after the oil had sat for several days. One 23 m³ (5000 gal) tank that contained a mixture of primarily untreated crude oil emulsion and the Bunker C took about one hour to pump out with a Spate 3-B pump; the other 23 m³ holding tank containing primarily Elastolized (800-1000 ppm) crude oil and emulsion was pumped for 3 hours with a Spate 3-B and finally for an additional 2 hours with a high capacity gear pump before it was emptied. The high back pressures developed by Elastolized oil when pumping after the oil has sat for some time is illustrated by the fact that on two occasions, the clamps on the discharge hose of a Spate 3-B failed while pumping Elastol-treated oil, and the fact that Elastol-treated oil caused the pump of a MI-30 skimmer to seize.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- * The Framo ACW-400 skimmer recovered oils and their emulsions with viscosities in the 10-300 cSt range at rates of 30 - 50 m³/hr; increasing disc speed and lowering the weir both increased recovery rate in this range. Recovery rates

decreased dramatically as the viscosity of the oil or emulsion increased above 1000 cSt, to 5 – 10 m³/hr at 10,000 cSt. Oil/emulsion content factors in calm conditions ranged from 75–90% with crude oils and emulsions and 75 – 88% for Bunker C. Increasing disc speed and lowering the weir both reduced the oil/emulsion content factor. Although the unit operated reliably throughout the trial and effectively in calm water, the device's propensity to strongly emulsify recovered oil and entrained water in its centrifugal pump and its pitching action in waves, detract from its overall performance as an offshore skimmer.

- * The GT-185 recovered oil and emulsion at a steady 25 – 30 m³/hr, regardless of viscosity in the range 10 – 10,000 cSt or wave action. Oil/emulsion recovery rates were in the 5 m³/hr range with Bunker C with a viscosity of some 90,000 cSt. Oil/emulsion content factors were consistently 90+% for crude oils and emulsions in both calm and wave conditions. Skimming of Bunker C gave oil content factors of 75 – 83% in calm conditions and 8 – 50% in waves. In general the skimmer operated well and reliably during the tests and followed waves well. Removal of the Light Oil Adapter, even with emulsion viscosities as high as 90,000 cSt, detracted from the skimmers performance.
- * The Walosep W-2 recovered a steady 14 – 16 m³/hr of oil and emulsion in the viscosity range 10 – 200 cSt. With very viscous (>100,000 cSt) Bunker C emulsion the recovery rate fell to 2 – 5 m³/hr. Oil/emulsion content factors were consistently in the 98+% range with crude oils and emulsions, falling to 17 – 47% with the viscous Bunker C emulsion. The device operated reliably, even though underpowered, throughout the tests and followed waves well.
- * The Heavy Oil Skimmer operated poorly in all tests, proving unable to recover oil without the addition of Elastol.
- * Despite the fact that temperatures during the tests were not low enough to cause the waxy oil to gel completely, the tests showed that the GT-185, Walosep W-2 and Framo ACW-400 should be able to recover slicks of relatively fresh waxy oils and their emulsions at peak summer water temperatures on the Grand Banks (12°C). The test results showed that oil/emulsion recovery rates, under these conditions, would be 30 – 40% less than for a conventional crude with the Framo ACW-400 and about the same, as for a conventional crude with the GT-185 and Walosep W-2 skimmers. Oil/emulsion content factors were reduced (i.e., more water was entrained) for the Framo ACW-400 and GT-185 skimmers when skimming waxy oil compared to conventional oil; oil/emulsion content factors for the Walosep W-2 remained unchanged. Based on visual observations of the skimmers operating early on in the waxy oil tests, the Walosep W-2 may be the best one for recovering gelled oil pieces at colder water temperatures on the Grand Banks.
- * The addition of Elastol to test oils and emulsions improved the oil/emulsion recovery rate of the Walosep W-2 by 15 – 40% (the former being the likely sustainable improvement), had no effect on the recovery rate but increased the water entrainment of the Framo ACW-400, and reduced the recovery rate of the GT-185 by 25 – 35% and increased its water entrainment rate. The addition of Elastol had several negative effects on subsequent downstream operations, including difficulty pumping and the level of effort required to clean Elastol-treated oil off equipment.

Recommendations

- * Consideration should be given to testing the floatability and stability of the Framo ACW-400 skimmer head vis-a-vis modifying it to operate as a free-floating skimmer.
- * The Light Oil Adapter for the GT-185 should be left in place during skimming operations, even with oil viscosities up to 100,000 cSt.
- * Consideration should be given to improving the weir adjustment lever on the GT-185 power-pack to allow finer control of the weir immersion.
- * Consideration should be given to modifying the Heavy Oil Skimmer to take advantage of its abilities to draw in Bunker C when operating in the downward rotation mode. The scraper blades should be spring-mounted for a smoother action.
- * Further testing of the Walosep W-2 and GT-185 skimmers with completely gelled waxy oil pieces is recommended. A suitable power-pack for the Walosep W-2 should be utilized.

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**OIL-BURNING TESTS CONDUCTED IN THE PRESENCE OF
A HIGH PRESSURE WATERJET BARRIER**

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and

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ABSTRACT

A series of burning tests were carried out in a 12m x 15m outdoor basin near Fleet Technology Limited's laboratory in Kanata. The tests were conducted in the presence of a prototype high pressure waterjet barrier that was previously produced by Environment Canada to investigate its effect on the volumetric and mass burn efficiency, and on the opacity of the smoke. It was found that the presence of the waterjet barrier reduced the opacity of the smoke. However, it contributed to the formation of emulsions which reduced the burn efficiency.

INTRODUCTION AND PROJECT OBJECTIVES

Over the past decade, considerable efforts have been expended towards the development of countermeasures that are effective for floating oil slicks.

Waterjets are one method that has been studied to herd and contain the spilled oil. Low pressure waterjets were tested as fireproof oil slick containment devices (Comfort, 1980). Subsequently, a system of high pressure waterjets was developed for oil spill control and a large prototype system was produced (Meikle et al, 1985; Meikle, 1983). This system has been deployed in the field (eg. Laperriere, 1985) and tested in the laboratory. Recently, tests have been done to optimize the mechanical configuration of the high pressure waterjets (eg. operating pressure, angle of incidence, nozzle spacing) for oil spill retention (Phillips et al, 1987).

However, the effect of the waterjet barrier on oil burning efficiency has not been tested. It was hypothesized that the waterjet barrier may also improve the combustion of the oil by providing greater aeration of the flame. Comfort, 1989 has recently conducted a project to improve present understanding of this issue.

The specific objectives of the test program were to:

- (a) evaluate the effect of the waterjet barrier on the volumetric and mass oil burn efficiency.
- (b) evaluate the effect of the waterjet barrier on the opacity of the smoke plume produced during the burn.

PROJECT SCOPE

Test Setup and Description

Test Facilities Burning tests were conducted in an outdoor basin near Fleet Technology Limited's laboratories in Kanata, Ontario. This basin was 12m x 15m in area and 0.5m deep. See Figures 1 and 2.

A high pressure waterjet system was supplied by Environment Canada for the tests and was operated by a technician from Sanivan Inc. during the project. The waterjet barrier was deployed in a "V" and a circle configuration, as shown in Figures 1 and 2 and Plates 1 and 2. The waterjet barrier is described subsequently.

Test Documentation Each test was documented using colour video photography and 35mm still photographs. Both black and white, and colour photographs were taken.

The following parameters were measured for each test:

- (a) Environment Data: Ambient Air temperature
Ambient Water temperature
Ambient Windspeed and direction
- (b) Oil Burn Data: Pre-burn weight and volume of the oil
Weight and volume of the residue
Density and reflectance of the smoke plume
Duration of burn
Flame temperature
Moisture content of the residue (for some tests)

The oil used for each test was placed in standard 200 litre (45 gal.) drums to determine the pre-burn weight and volume. For the first test, the weight of the oil was measured using a large balance beam scale and the volume was measured using a linear scale. See Figure 3 for schematic. These measurements were used to determine the pre-burn weight and volume of the oil for subsequent tests.

At the end of each test, the residue was collected using a combination of pails and shovels. With this collection approach, some water was picked up with the oil. The residue was placed in an oil drum and the water was drained through an outlet at the base of the drum. See Figure 3 for schematic.

After the water had been drained, the volume of the residue was measured using a linear scale and the weight was measured using a large balance beam scale.

Measurements were also made to determine the opacity of the smoke plume. The reflectance of the smoke plume was measured using a Pentax Spotmeter V and a Pentax Gray Card (of 18% reflectance). The luminance of both the plume and the card were measured for each test. Typically, the luminance of the smoke plume was measured near the centre of the plume. These data were used to determine the illuminance just before the test was commenced and the reflectance of the plume.

These data were also related to standard smoke densities shown by measuring the reflectance of the grey shades shown in Figure 4.

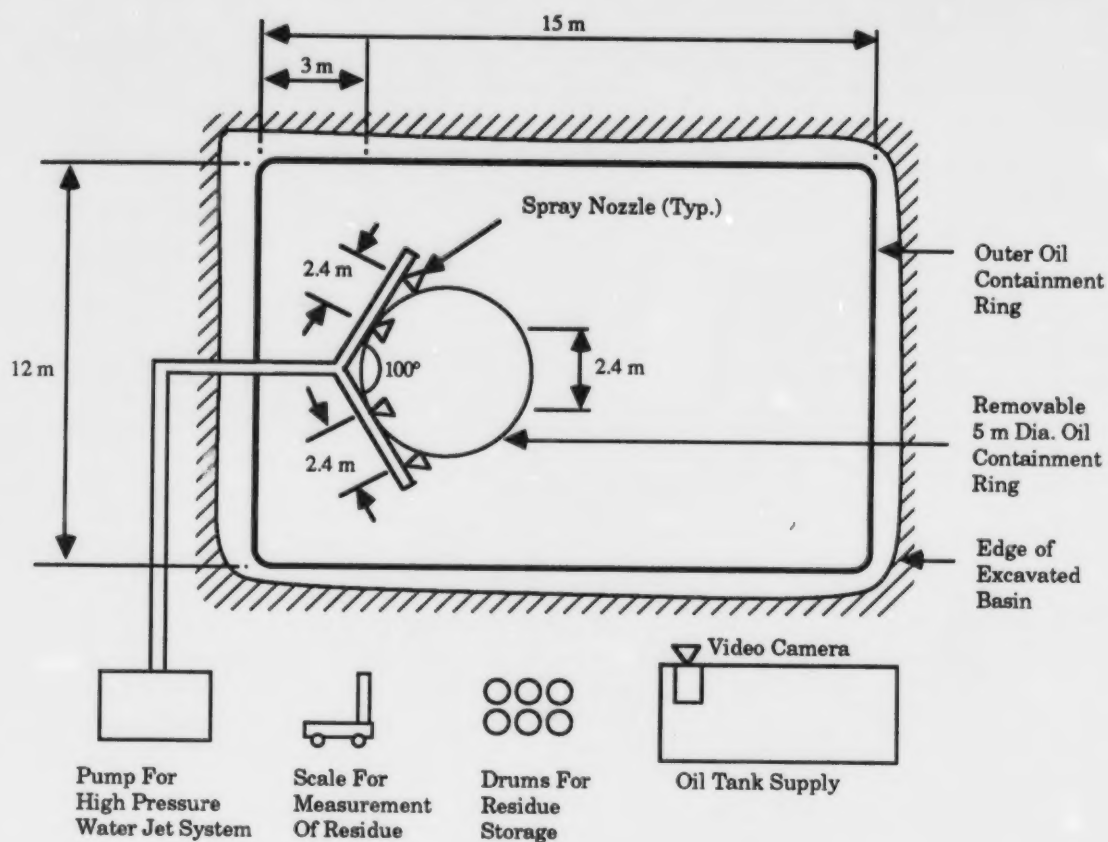


Figure 1a Schematic of Test Setup - Waterjet Barrier Configuration "V"

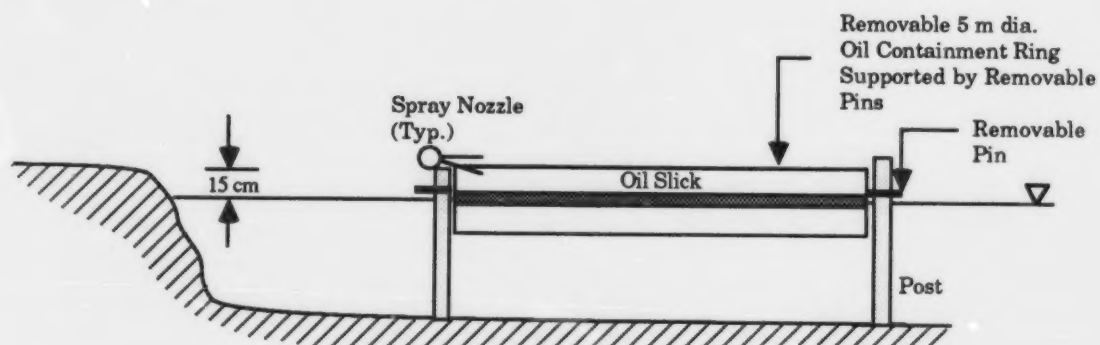


Figure 1b Cross-sectional View: "V" Configuration

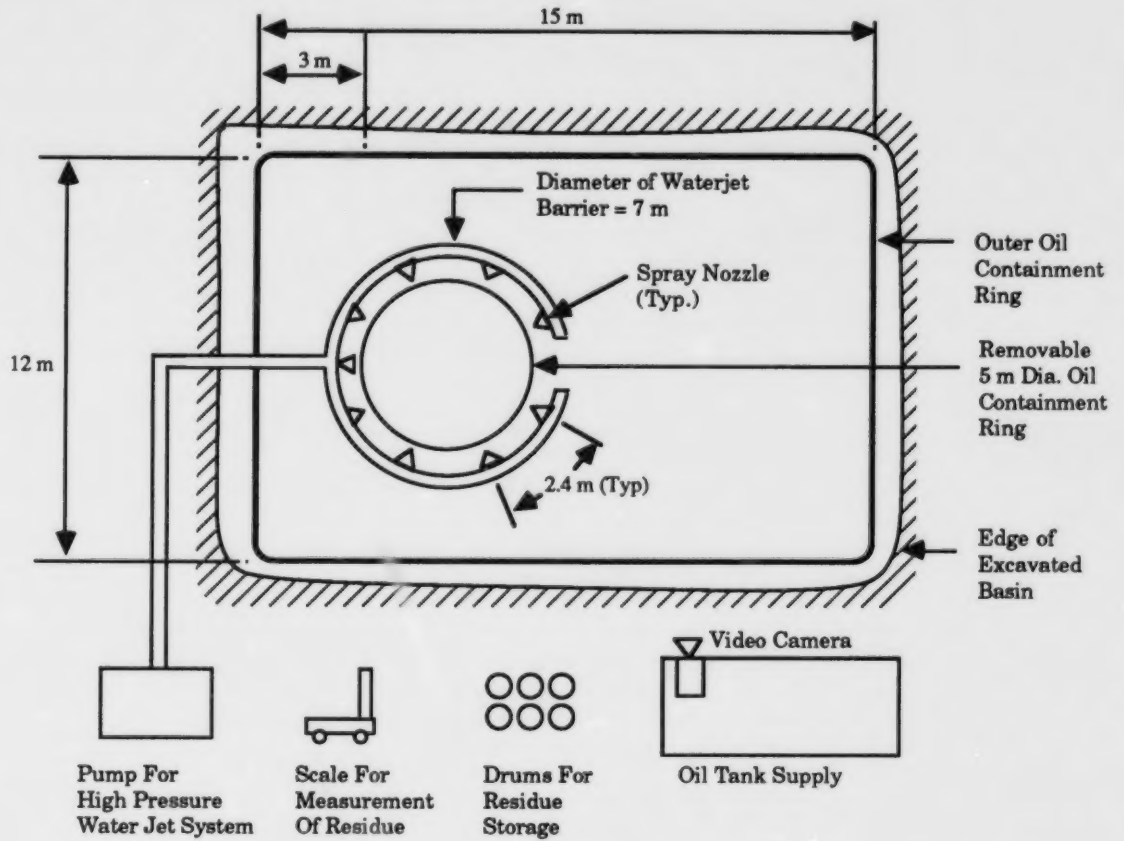
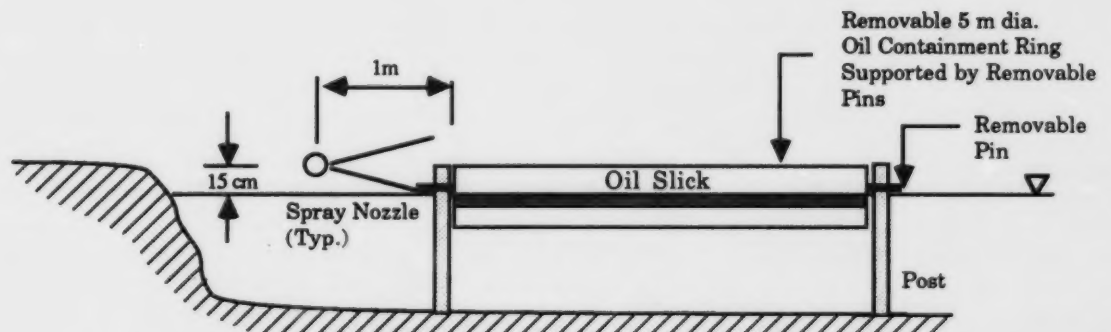


Figure 2a Schematic of Test Setup - Waterjet Barrier Configuration: Circle



Note: Centreline of waterjet kept at same elevation as top of containment ring.

Figure 2b Cross-sectional View: Circle Configuration

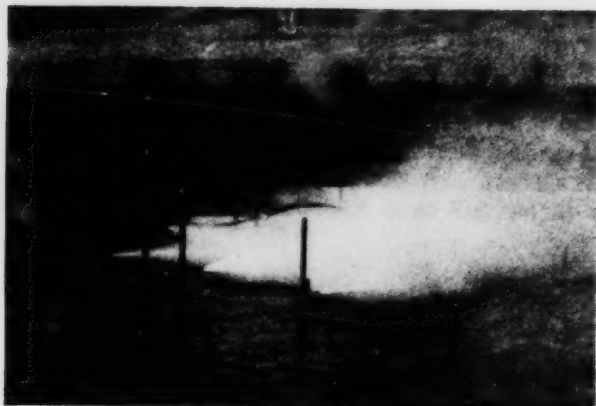


Plate 1

Waterjet Barrier in
"V" Configuration



Plate 2

Waterjet Barrier in
Circle Configuration



Plate 3

Ignition of Oil Slick

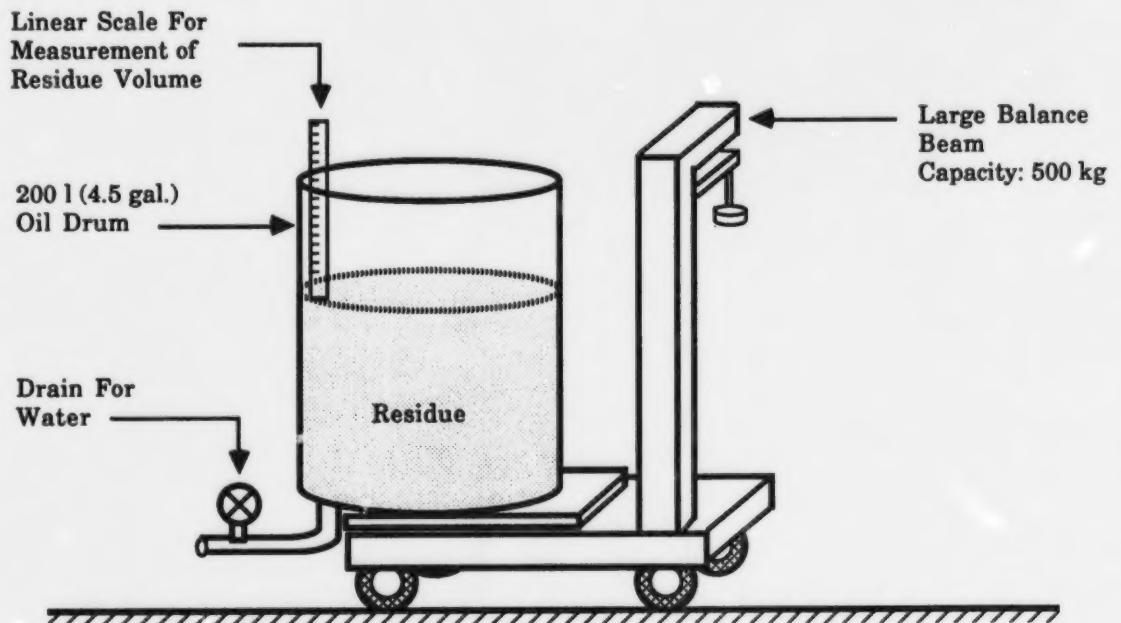


Figure 3 Schematic of Setup For Measurement of Weight and Volume of Residue

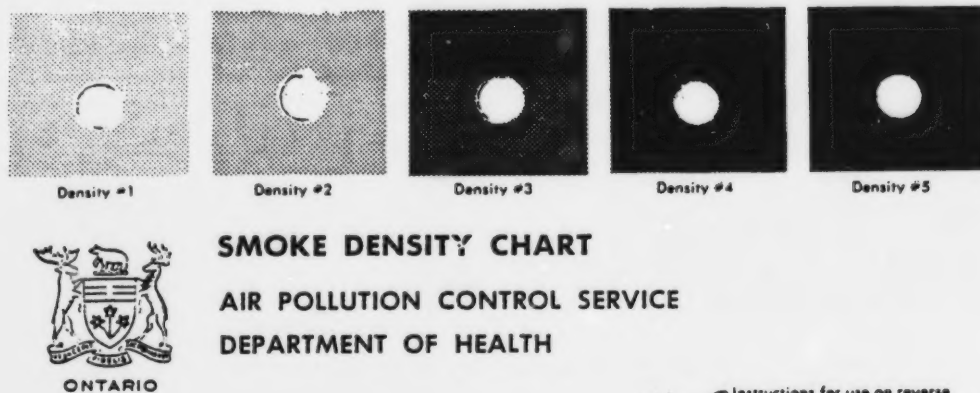


Figure 4 Smoke Density Chart

Waterjet Barrier As outlined in the first section, a large, prototype, high pressure waterjet barrier system has been developed and produced by Environment Canada. This prototype system was used in this project.

The setup of the waterjet barrier selected for these tests was based on the results of previous tests to optimize the performance of the system (Phillips et al, 1987) and on previous operating experience (e.g. Laperriere, 1985).

The table below describes some key setup parameters for the waterjet barrier:

Nozzle:	No. 6530
	Spread angle: 65°
	Aperture: 0.13 in.
	Vertical angle between jet and water surface: 10°
Operating Pressure:	See following text.
Height of Nozzles:	15-30cm
Spacing of Nozzles:	2.5-3m
Configuration of Waterjet Barriers:	"V" and "circle" as shown in Figures 1 and 2.

It was initially planned to operate the waterjet barrier at the same pressure used during previous laboratory tests (Phillips et al, 1987) and field deployment (e.g. Laperriere, 1985). The range of operating pressures tested in the laboratory by Phillips et al, 1987 was 6.9 to 20.7 mpa (1000 to 3000 psi). During a field deployment at Norman Wells, NWT, Laperriere, 1985 operated the waterjet barrier at 5.9 mpa (850 psi) and 9.0 mpa (1300 psi) in the deflection mode and at 9.7 mpa (1400 psi) in the collection mode.

During our tests, it was found that the operation of the waterjet barrier at pressures in excess of 6.9 mpa (1000 psi) caused a noticeable reduction in the extent of the flame which would have resulted in the eventual extinction of the flame. Furthermore, it was found that the oil became emulsified in the presence of the waterjet.

Consequently, it was decided to operate the waterjet barrier at lower pressure for our tests.

The maximum operating pressure for these tests ranged from 0.7 to 6.9 mpa (100 to 1000 psi). These tests were conducted by instructing the technician operating the waterjet barrier to maximize the length of the burn. Efforts were made to operate the waterjet barrier at the pressure which provided maximum aeration of the flame. This was judged by the colour of the smoke and efforts were made to keep the smoke as clear as possible. When it was clear that the extent of the flame was being reduced by the jet, the pressure of the waterjet barrier was reduced and the flame was allowed to build. This sequence was repeated until the burn was complete and the flame was extinguished. Efforts were not made to relight the oil after the flame was extinguished.

As will be discussed, the opacity of the smoke was significantly affected by the operation of the waterjet barrier. Special care was taken to operate the waterjet barrier so that the aeration of the flame was maximized, and hence the density of the plume was minimized. Thus, the results of this test program can be expected to overestimate the probable reduction in smoke density that would be achieved in a field deployment.

Oil Properties Table 1 summarizes the available data to describe the properties of the oil used during the tests.

These properties were confirmed by Environment Canada who undertook analyses of oil samples collected during the test program.

TABLE 1
SUMMARY OF OIL PROPERTIES

Published Data by Gaiswinkler Enterprises Limited

Oil Type:	Ontario Light Crude Oil			
Oil Properties:	Specific gravity at 60°F	:	0.816	
	A.P.I. gravity at 60°F	:	41.9	
	Sulphur percent (by wt)	:	0.18	
	Pour point	:	15°F	
	Colour	:	greenish black	
	Carbon residue percent (by wt)	:	1.0	
	Saybolt universal viscosity at 100°F	:	39 sec.	

Results of Oil Analyses Undertaken by Environment Canada

Density	:	0.8234 g/cc
Viscosity at 60°F	:	5.8 cps

Environmental Conditions Efforts were made to conduct all of the tests in conditions of zero precipitation and low windspeeds.

Table 2 summarizes the environmental conditions for each test.

TABLE 2
SUMMARY OF ENVIRONMENTAL CONDITIONS

Test #	Air Temp. (°C)	Water Temp. (°C)	Ambient Windspeed (m/s)		Precipitation
			Avg.	Peak	
1	3.5	2.3	1.8	2.7	Nil
2	5.0	3.5	2.5	3.0	Nil
3	10.0	8.0	4.0	8.0	Nil
4	11.0	9.0	4.0	6.0	Nil
5	10.0	9.0	4.0	6.0	Nil
6	5.0	5.0	1.7	2.2	Nil
7	6.0	6.0	Nil	Nil	Nil
8	2.0	3.0	2.0	3.1	Nil
9	10.0	4.5	1.3	1.5	Nil
10	6.5	6.0	0.3	0.3	Nil
11	3.0	4.5	3.0	4.3	Nil
12	7.0	6.0	2.7	3.7	Nil

Test Matrix

The following parameters were systematically varied during the test program:

- (a) the configuration of the waterjet barrier. Tests were carried out with the waterjet barrier deployed in a "V" and a circle as described earlier. Also, some tests were carried out without the waterjet barrier.
- (b) the thickness of the oil slick.
- (c) the containment provided to the oil slick. The oil slick was either "contained" in a 5m diameter ring or "uncontained".

A total of 12 tests were carried out. The test matrix is summarized in Table 3.

TABLE 3
TEST MATRIX

Test #	Test Date	Mean Thick. of Oil Slick (mm)	Oil Slick Contained In Ring?	Waterjet Barrier		Configuration	
				Not Operating		"V"	Circle
1	Nov. 4	9.9	Yes			✓	
2	Nov. 4	19.8	Yes			✓	
3	Nov. 6	19.8	Yes	✓			
4	Nov. 6	9.9	Yes	✓			
5	Nov. 6	9.9	No	✓			
6	Nov. 8	9.9	No			✓	
7	Nov. 8	19.8	No			✓	
8	Nov. 15	9.9	Yes				✓
9	Nov. 15	19.8	Yes				✓
10	Nov. 15	9.9	Yes				✓
11	Nov. 16	9.9	No				✓
12	Nov. 16	19.8	No				✓

TEST RESULTS

Qualitative Description of the Tests

Test Without the Waterjet Barrier Tests 3, 4 and 5 were done with the waterjet barrier shut off. These tests were done to provide a baseline against which the effects of the waterjet barrier would be measured.

For Tests 3 and 4, the oil was contained in the ring, and hence, the burn was confined to the ring.

Test 5 was an uncontained test. However, the oil was herded by wind action to the end of the tank before it could be ignited. The estimated size of the slick at the time of ignition was 40m² and the mean oil slick thickness was computed to be 5mm. After the oil slick was ignited, the burn was confined to the area initially occupied by the slick.

Each of these burns was very rapid (with a burn duration of 5-6 minutes) and produced a large amount of black, dense smoke. See Plate 4 for a typical burn.



Plate 4

Test #5

Plate 5

Test #2

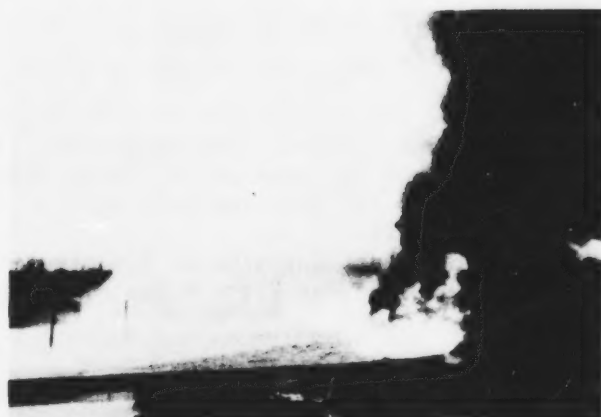


Plate 6

Test #6



Plate 7

Test #8

Plate 8

Test #11

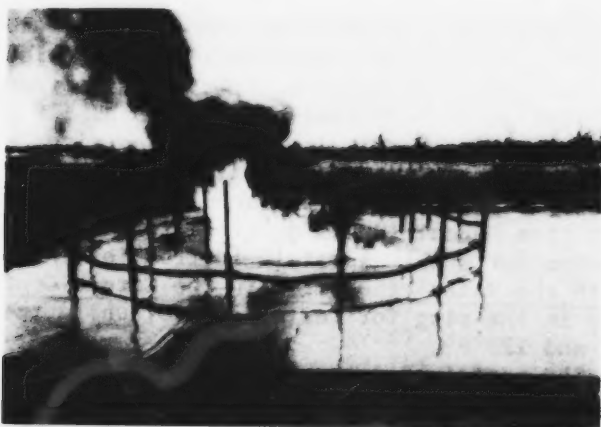


Plate 9

Test #12

Tests With the Waterjet Barrier in the "V" Configuration The oil was contained in the ring for Tests 1 and 2, while the oil was uncontained for Tests 6 and 7.

For the contained tests, the oil was placed inside the ring and ignited. The waterjet barrier was then activated which pushed the burning oil slick towards the outer edge of the ring. The burning oil slick was estimated to cover about two thirds of the area inside the ring after the waterjets were activated. These burns were of long duration (i.e. 36 and 82 minutes) and the waterjets produced a noticeable reduction in smoke opacity. Plate 5 shows a typical burn.

For the uncontained tests, the oil was placed inside the ring and ignited. The waterjet barrier was then activated and the containment ring was dropped to the bottom of the basin.

For these tests, the burning oil was pushed to the end of the basin by the waterjets. For Test 6, the burn was confined to an estimated area of 40m^2 . The mean oil slick thickness over this area was computed to be 5mm. See Plate 6. For Test 7, the containment ring was obstructed and did not drop cleanly to the bottom. This caused the oil slick to be more dispersed by the action of the waterjet (than was the case for Test 6). However, soon after the ring was dropped, the oil slick was pushed towards the outer ring of the basin and was contained there for the remainder of the burn.

The uncontained burns (i.e. Tests 6 and 7) were very similar to the uncontained burn conducted with the waterjet barrier shut off (i.e. Test 5). The duration of burns 6 and 7 was very short (i.e. 7 and 5 minutes respectively) in comparison to a burn duration of 5 minutes for Test 5. Furthermore, burns 6 and 7 produced a large amount of dense, black smoke, which appeared similar to that produced by burn 5. In general, it appeared that the influence of the waterjets on the burn was minor and that the main effect of the waterjets during these uncontained tests was to herd the oil towards the end of the basin. The edge of the oil slick was relatively distant from the waterjets (i.e. about 10m) and little turbulence was produced by the waterjets on the water surface immediately in front of the slick perimeter.

Tests With the Waterjet Barrier in the Circle Configuration The oil was contained in the ring for Tests 8 to 10, while the oil was uncontained for Tests 11 and 12.

For the contained tests, the oil was placed inside the ring and ignited. The waterjet barrier was then activated which pushed most of the burning oil slick towards the centre of the ring into a circular slick about 3m in diameter. However, some oil remained near the outer edges of the ring as it was not contacted by the waterjets. Eventually, the oil near the edge of the ring was moved to the centre area by the surface currents induced by the waterjets. See Plate 7 for a typical burn.

The flame in the central portion of the ring was aerated by the waterjets and the smoke was light-coloured. The oil which had remained near the edges of the ring burned with a noticeably denser, black smoke.

Emulsions were formed during these tests. There was an especially large amount of residue from Test 8 (i.e. 195% and 220% of the volume and weight of the spilled oil, respectively). Consequently, this test was repeated (as Test 10). However, for Test 10, the maximum operating pressure of the waterjet barrier was reduced to 0.7mpa (100 psi) from 2.1mpa (300 psi) for Test 8. This was found to reduce the residue somewhat. For Test 10, the weight and volume of the residue was 114% and 120% of that of the spilled oil, respectively.

The uncontained tests (i.e. Tests 11 and 12) were conducted by placing the oil in the ring, igniting the oil, activating the waterjet barrier, and then dropping the containment ring to the bottom of the basin. For these tests, some of the oil escaped past the waterjet barrier when the containment ring was dropped. The oil which escaped was contained by the outer ring of the basin. Most of it was eventually moved back inside the circular waterjet barrier by the surface currents produced by the waterjet barrier where it was burned.

Thus, the burn was comprised of oil that was inside the waterjet barrier, which produced smoke that was light-coloured, and oil that was beyond the waterjets, which produced dense, black smoke. See Plates 8 and 9.

Quantitative Test Results

Tables 4, 5 and 6 summarizes the quantitative data that were measured during the test program.

SUMMARY AND CONCLUSIONS

Summary

(i) Burn Efficiency:

- (a) The operation of the waterjet barrier significantly increased the weight and volume of the residue (in comparison to tests done without the waterjet barrier). This is summarized below:

Oil Slick Contained in Ring?	Waterjet Barrier Configuration		Residue as a Percentage of the Spilled Oil	
	Not Operating	"V" Circle	By Volume	By Weight
Yes	✓		11-25	10-22
No	✓		9	9
Yes		✓	16-67	15-61
No		✓	27-42	24-39
Yes		✓	37-195	39-220
No		✓	22-53	24-57

The operation of the waterjet barrier was found to produce turbulence on the water surface and to cause the formation of emulsions. This is believed to be the principal reason for the observed reduction in burn efficiency.

- (b) During the tests, care was taken to operate the waterjet barrier to minimize the formation of emulsions as follows:
- The waterjet barrier was operated at relatively low pressures (i.e. a maximum of 0.7 to 6.9mpa over the duration of the tests). These pressures are significantly less than the pressure (of about 14mpa) that previous laboratory tests had shown to provide maximum oil slick retention capability without emulsifying the oil.
 - For the tests in which the waterjet barrier was deployed in a circle and the oil slick was contained, the waterjets were set up to avoid direct impingement on the oil. The waterjets were positioned such that they just cleared the top of the containment ring.

TABLE 4
SUMMARY OF OIL BURN DATA

Test #	Maximum Operating Pressure of Waterjet Barrier (mpa)	Burn Duration (min.)	Flame Temperature (°C)
1	6.9 (1000 psi)	36	1290
2	2.8 (400 psi)	82	1260 - 1510
3	Waterjet Barrier Off	6	1350
4	Waterjet Barrier Off	5	1550
5	Waterjet Barrier Off	5	1500
6	4.8 (700 psi)	7	1200
7	6.9 (1000 psi)	5	1400
8	2.1 (300 psi)	10	1400
9	0.7 (100 psi)	28	1590
10	0.7 (100 psi)	12	1500
11	2.1 (300 psi)	30	1400
12	2.1 (300 psi)	34	1400

TABLE 5
SUMMARY OF OIL BURNING EFFICIENCIES

Test #	Spilled Oil		Residue Remaining After Burn		Residue as a Percentage of the Spilled Oil		Moisture Content of Residue ⁴	
	Vol. (l)	Wt. (kg)	Vol. (l)	Wt. (kg)	By Volume	By Weight	% by weight	Maximum Variance
1	194	171	130	104	67	61	No data	
2	388	342	61	50	16	15	No data	
3	388	342	43	33	11	10	No data	
4	194	171	48	38	25	22	No data	
5	194	171	17	15	9	9	No data	
6	194	171	82 ³	66 ³	42 ³	39 ³	No data	
7	194	171	52 ³	41 ³	27 ³	24 ³	No data	
8	194	171	379 ¹	376 ¹	195 ¹	220 ¹	23	7
9	388	342	142 ¹	135 ¹	37	39	28	5
10	194	171	222 ¹	219 ¹	114 ¹	128 ¹	14	2
11	194	171	103 ²	97 ²	53 ²	57 ²	18	6
12	388	342	84 ²	83.5 ²	22 ²	24 ²	3	1

Notes:

- Test 10 was a repetition of test 8. For test 10, the waterjet barrier was operated at a maximum of 100 psi (versus a maximum pressure of 300 psi for test 8).
- These tests were uncontained with the waterjet barrier in a circle configuration. Oil escaped under the waterjet barrier and was contained by the outer ring. Some of the oil which escaped burned outside of the waterjet barrier. The remainder was moved back inside the waterjet barrier by the induced surface currents.
- These tests were uncontained with the waterjet barrier in a "V" configuration. The oil was pushed by the waterjets to the end of the basin where it was contained by the outer ring. The estimated mean thickness of the oil slick at the start of the test was 5mm.
- These oil analyses were undertaken by Environment Canada.

Table 6
Summary of Smoke Opacity Data

Test #	Luminance of Std.		Illuminance		Luminance of Smoke Plume		Reflectance of	
	18% Reflectance	Spotmeter	Spotmeter	(Foot-Lamberts)	Spotmeter	(Foot-Lamberts)	Smoke Plume	Smoke Density ²
	Rdg. (EV)	(Foot-Lamberts)	Rdg. (EV)		Rdg. (EV)		(%)	
1	10.2	46	256	10.5	60	23	4	4
2	9.0	21	117	8.0	10.5	9	5	5
3	12.3	210	1170	10.0	42	4	5	5
4	12.7	270	1500	9.5	30	2	5	5
5	14.0	670	3720	12.0	165	4	5	5
6	10.6	64	360	8.6	16.5	5	5	5
7	12.0	165	920	8.5	16	17	4-5	
8	15.2	1450	8060	13.3	420	5	5	
9	14.6	1000	5600	14.1-15.5 ¹	700-1600	12-29	3-5	
10	10.7	66	370	11.5	120	32	3-4	
11	11.4	110	610	10-13 ¹	41-330	7-54	2-5	
12	13.5	460	2560	10.5-14.5 ¹	60-900	2-35	3-5	

Notes: 1. The smoke plume was alternately light and dark depending on the operation of the waterjet barrier.

2. See Figure 4 for definition of smoke density.

On the other hand, the tests were done on a relatively small scale. For a large burn in the field, the formation of emulsions (produced by the action of the waterjet barrier) is expected to be localized at the perimeter with the result that higher burn efficiencies may be achieved.

Thus, the results of this test program may underestimate the burn efficiencies that would be achieved in a field deployment.

- (c) The burn efficiency increases significantly with the slick thickness. For the tests done with a mean slick thickness of 19.8mm, the weight and volume of the residue (expressed as a percentage of that of the spilled oil) was about one quarter of that left from the burns done with a mean slick thickness of 9.9mm.
- (d) The weight and volume of the residue was increased when the waterjet barrier was deployed in a circle for the contained tests (in comparison to the "V" configuration). This is believed to reflect increased emulsification of the oil for the circle configuration.
- (e) For the uncontained tests, the circle and "V" configurations produced residues that approximately equal in weight and volume. This is believed to reflect the fact that some of the oil escaped past the waterjet barrier in the circle configuration.
- (f) The uncontained tests were not free from edge effects as the oil was contained by the outer ring of the basin. It is expected that the oil slick would have been more dispersed in a field deployment and that the burn efficiency would be lowered. This would cause these test results to overpredict the burn efficiency that would be achieved in a field deployment.

(ii) Smoke Opacity:

- (a) The operation of the waterjet barrier was found to reduce the opacity of the smoke, as summarized below:

Oil Slick Contained in Ring?	Waterjet Barrier Configuration			Reflectance of Smoke Plume (%)	Smoke Density Level**
	Not Operating	"V"	Circle		
Yes	✓			2-4	5
No	✓			4	5
Yes		✓		9-23	4-5
No		✓		5-17	4-5
Yes			✓	5-32	3-5
No			✓	2-54	2-5

**Figure 4 for a definition of the "smoke density level".

- (b) The results of this test program are expected to overestimate the probable reduction in smoke opacity that could be achieved by the use of the waterjet barrier in a field deployment as:
- special care was taken to operate the waterjet barrier to maximize the length of burn.
 - the tests were done on a relatively small scale which allowed the waterjet barrier to provide relatively good aeration over the whole flame area.

Conclusions

The test program has provided data and observations for a preliminary assessment of the effect of a waterjet barrier on the burn efficiency of a floating oil slick.

The following conclusions are drawn from this test program:

- (a) the operation of the waterjet barrier increased the volume and weight of the residue (in comparison to the tests done without the waterjet barrier) as it caused the formation of emulsions.
- (b) the operation of the waterjet barrier reduced the opacity of the smoke.

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**DISPOSAL OF SPILLED HIBERNIA CRUDE
OILS AND EMULSIONS**

**IN-SITU BURNING AND THE
"SWIRLFIRE" BURNER**

by

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This study was a continuation of previous work (S.L. Ross 1988) on combustion techniques for the disposal of recovered oily materials from spill cleanups. The present study focused on two subject areas identified earlier as requiring further research and development, namely: in-situ burning of Grand Banks' crude oils and their emulsions on water and testing of a novel rotary-cup burner for the disposal of oil and emulsions recovered by skimming operations.

OBJECTIVES

The two objectives of the study were:

- * to conduct small-scale tests of in-situ burning of Grand Banks crude oils and their emulsions to determine the effect of weathering and emulsion water content on their ignitability, removal efficiency and removal rate; and
- * to test a prototype of the "Swirlfire" rotary cup burner to determine the effect of oil type, weathering and emulsion water content on its ability to dispose of oils recovered by skimming operations.

PAPER CONTENTS

Although related, the two subject areas of the study were distinct from each other in objective, experimental techniques and product. As such, this paper contains separate accounts of the methods and results of each subject. The in-situ burning tests are presented first followed by the rotary cup burner tests. The conclusions and recommendations are combined at the end of the paper.

IN-SITU BURNING OF HIBERNIA CRUDE OILS AND EMULSIONS

EQUIPMENT AND METHODS

The Oils

Two oils discovered on the Grand Banks were used for this study, Hibernia B-27 and Hibernia C-96. The physical properties of these oils are listed in Table 1. The B-27 crude is a medium gravity crude that exhibits moderately waxy characteristics; the C-96 crude is a light gravity crude that exhibits very waxy characteristics. Portions of each oil were weathered by air sparging to simulate evaporative loss when spilled. For the C-96 crude, samples were weathered to 5 and 10% loss by weight, equivalent to evaporative exposures (Stiver and Mackay 1983) of about 4000 and 40,000 respectively or about 1.25 and 12 hours at sea for a 5 mm thick slick in a 5 m/s wind at 10°C (S.L. Ross and DMER 1988). Portions of the B-27 crude were similarly weathered to 8 and 14% mass loss (equivalent to exposures of the C-96 oil).

TABLE 1

Physical Properties of the Hibernia Crude Oils
Used for the In-Situ Burning Tests

OIL	DENSITY (kg/m ³)			VISCOSITY (mPas)			POUR POINT (°C)	FLASH POINT (°C)
	@10°C	@20°C	@30°C	@10°C	@20°C	@30°C		
HIBERNIA C-96	844	837	830	*	90	30	18	14
HIBERNIA B-27	878	870	862	240	80	25	9	11

* below pour point
from S.L. Ross and DMER 1988

Artificial water-in-oil emulsions were prepared for each fresh and weathered oil sample by adding appropriate volumes of fresh water to oil in a mixer to produce 25%, 50% and 75% water emulsions. The emulsions were stirred vigorously until a homogeneous mixture, containing small water droplets, was created.

The Test Apparatus

The test burns were conducted in an 28 cm diameter metal ring supported in a 1 m diameter, 40 cm deep pan of water. This pan was situated under a hood connected to a roof-mounted vent fan (Figure 1). The freeboard of the ring was 1 cm to avoid creating vortices in the air drawn into the burns.

Test Measurements

The weight of a measured volume of oil or emulsion (required to create a 2, 5 or 10 mm thick slick in the metal ring) was determined with a triple beam balance. The weight of residue left after each test burn was determined by recovering the residue

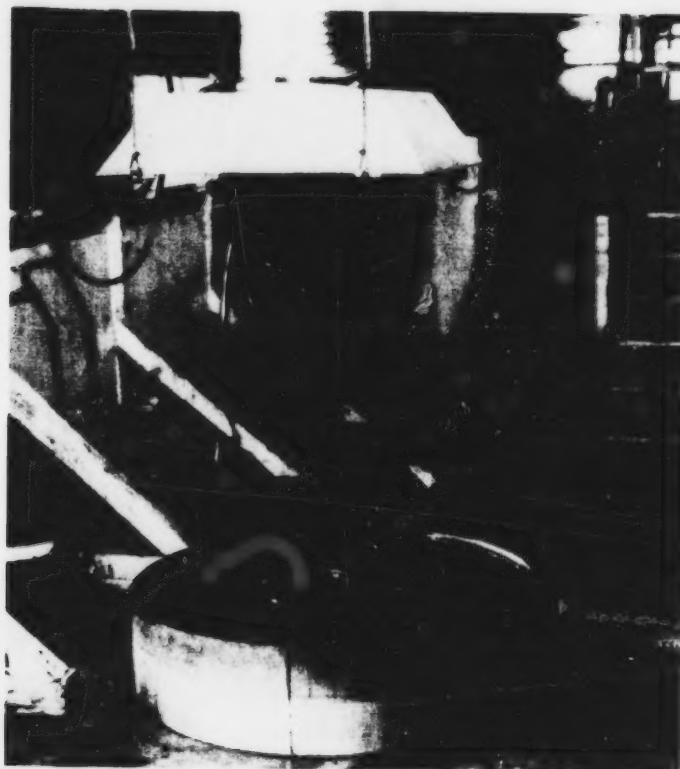


Figure 1 - In-situ
burning apparatus



Figure 2 - Balance, graduated cylinder and sorbent pad

on a preweighed sorbent pad, shaking out any water, then weighing the pad on the balance (Figure 2).

Ignition times (the time required for the entire surface area of the slick to catch fire) and burn time (the incremental time from complete ignition to flame extinction) were measured with a stopwatch. Each burn was also videotaped.

Ignition Techniques

Three increasing levels of ignition were available for use on each test. First, a 5 cm square of sorbent pad saturated with about 15–20 grams of fresh crude was lit and placed in the centre of the test slick (Figure 3). This burned for about 1 minute. If the slick had not ignited after this, a 10 cm square piece of sorbent containing about 45–50 grams of oil was lit and placed in the centre of the test slick (Figure 4). This burned for about 2 minutes. If the slick had still not ignited after this, 120 ml (equivalent to 2 mm thick) of fresh crude was poured on top of the test slick and ignited. If, after 2 minutes (the approximate time for the 120 ml of fresh crude to be consumed), the flames extinguished the test slick was denoted as unignitable.

The sizes of the pieces of saturated sorbent were specifically selected to represent sizes of burning globules of gelled gasoline produced by the "Helitorch" aerial ignition system (Spiltec 1987; S.L. Ross 1988) for ignition of oil slicks.

The 5 cm square represented the minimum size of globule required to achieve ignition of oil under relatively calm conditions (winds less than 16 km/hr).

The 10 cm square represented the minimum globule size to achieve ignition of oil in winds up to 30 km/hr and the average size of globules produced by the "Helitorch" system when rigged for oil slick ignition.

The use of 120 ml of burning fresh crude as a final attempt at ignition was designed to determine whether or not the oil or emulsion could be sufficiently preheated to support combustion. This would be analogous to oil or emulsion being swept into a fireproof boom in which oil is already burning (e.g., Buist et al. 1983; Allen 1989).

Test Procedures

The following procedure was followed for each test:

1. measure out required volume of oil or emulsion into graduated cylinder;
2. weigh cylinder;
3. pour oil or emulsion gently onto water inside metal ring;
4. spread oil evenly over water surface;
5. allow oil to cool to water temperature (10–13°C) and gel;
6. reweigh graduated cylinder;
7. start television camera;
8. light 5 cm square oil-soaked sorbent pad and place in centre of test slick;
9. record time for flames to cover entire test slick area;
10. if ignition fails repeat 8 and 9 with 10 cm square oil-soaked sorbent pad and then 120 ml fresh crude;
11. record time when flames extinguish;



Figure 3 — 5 cm square oil-soaked sorbent pad used for first ignition attempt



Figure 4 — 10 cm square oil-soaked sorbent pad used for second ignition attempt

12. recover oil residue on water outside ring and weigh sorbent pad;
13. recover oil residue on water inside ring and weigh sorbent pad;
14. pick up ring and swirl in pan to remove warm water and replace with cold.

RESULTS AND DISCUSSION

The report (S.L. Ross 1989) contains the conditions of and results for the 53 tests conducted.

Ignition Times

Figure 5 illustrates the effect of weathering on ignition time (defined as the time required for the flame to spread to cover the entire area of the slick) of unemulsified oils at the test temperature (10–13°C). In general, there was a slow increase in ignition time (i.e., reduction in flame spreading velocity) with increasing evaporative loss. The B-27 crude generally ignited faster than the C-96 crude. In all cases, ignition of the unemulsified oil was accomplished with the 5 cm square sorbent pad.

Figure 6 shows the effect of emulsification on ignition time. Ignition times for the fresh and 5% weathered C-96 crude increased from the 25–50s range with no water to the 50–75s range with the incorporation of 25% water in an emulsion. The ignition time for the 10% weathered C-96 crude increased from the 25–75s range with no water to the 250–500s range with a 25% water emulsion. The 2 mm thick slick of 10% weathered C-96 25% water emulsion could not be ignited.

At 50% water content, none of the C-96 test slicks could be ignited, except the 5% weathered oil which burned for a short while after the addition of 120 ml of fresh oil to 5 and 10 mm thick slicks. Needless to say it was not possible to ignite the 75% water content C-96 slicks.

Ignition times for the B-27 crude showed a less dramatic increase with emulsification. In the case of the fresh B-27 ignition times increased from the 25–50s range with both no emulsification and 25% water to the 80–100s range with 50% water. The 10 mm thick fresh, 75% water emulsion could only be ignited with the addition of 2 mm of fresh crude. The 8% weathered B-27 crude had ignition times in the 25–35s range with no emulsification, in the 50–110s range with 25% water and in the 115–135s range with 50% water. The 10 mm thick, 8% weathered emulsion with 75% water was successfully ignited with a 10 cm square oil soaked sorbent over a period of 344s. The 14% weathered B-27 had ignition times in the 30–45s range with no emulsification, in the 65–100s range with 25% water and in the 150–270s range with 50% water. The 75% water emulsion was almost fully ignited with a 10 cm square sorbent (it burned over 60% of the slick area for 326s) but required the addition of 2 mm of fresh crude for full ignition.

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FIGURE 5

EFFECT OF WEATHERING ON IGNITION

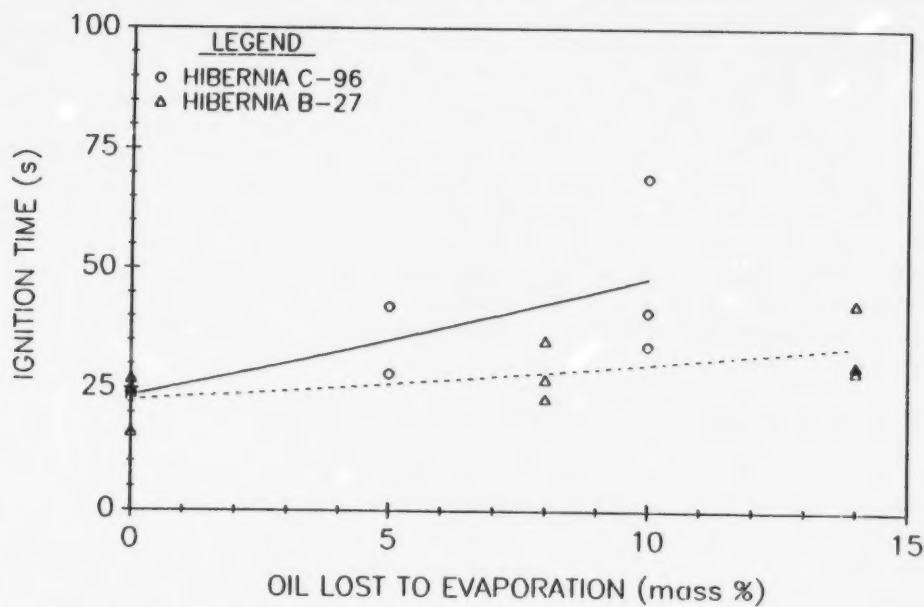
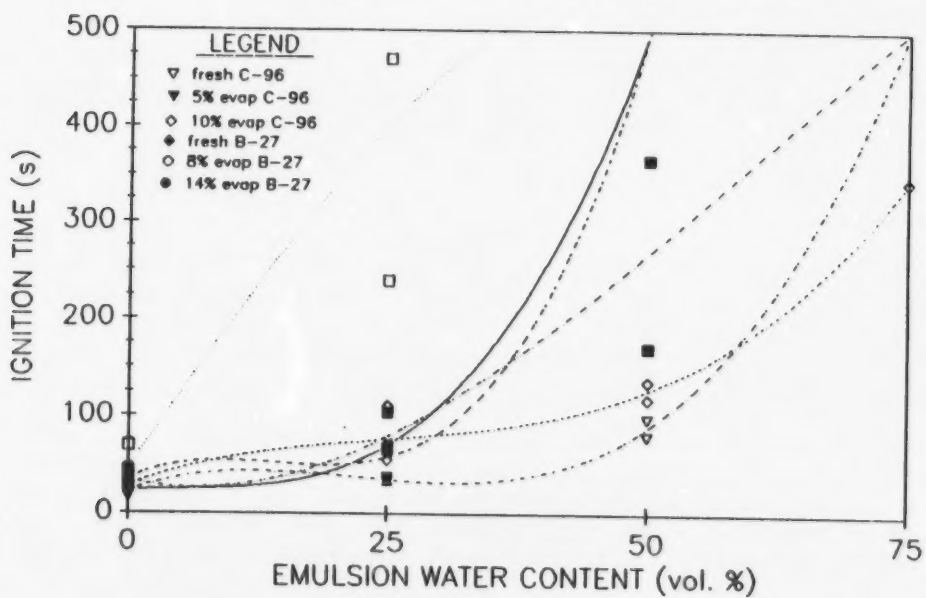


FIGURE 6

EFFECT OF EMULSION WATER CONTENT ON IGNITION



Ignition Source

Table 2 documents the success or failure of each of the three possible ignition sources (5 or 10 cm square oil-soaked sorbent or 2 mm of fresh crude) for the combinations of oil type, slick thickness, weathering and emulsion water content tested. The results indicate that the "Helitorch" aerial ignition system should be able to ignite relatively fresh (up to 12 hrs at sea) C-96 crude and emulsions with water contents in excess of 25% but less than 50%. Emulsions of C-96 with water contents in the 50% range and greater required the addition of fresh oil for any chance of ignition. In the case of the B-27 crude, the "Helitorch" should be able to ignite relatively fresh crude and emulsions with water contents up to 50%. Emulsions with 75% water required the addition of 2 mm of fresh oil, except in the case of the 8% weathered case which was successfully ignited with a 10 cm square sorbent.

Ejected Oil During Combustion – Effects on Burn Calculations

During the combustion process, heat radiated from the flame is transferred to the slick and from there to the underlying water. In the case of an unemulsified oil, when the slick has burned down to a thickness thin enough that the underlying water boils, droplets of oil are ejected into the flame by the rapid vaporization of the water (Figure 7). When emulsions are burned a similar process of rapid vaporization of the water droplets causes droplets of emulsion to be ejected into the flame throughout the burn process (Figure 8). The amount of oil ejected that escapes the flame (i.e., does not either burn completely in its trajectory or does not land back on the burning slick) is much greater when burning emulsions (Figure 9) rather than pure oil (Figure 10). Whether or not this ejected oil is included in determining burn efficiency affects the calculated burn efficiency and rate. Figure 11 compares the calculated burn efficiency for unemulsified oil both including and excluding the ejected oil (i.e., the mass of oil outside the metal ring after the burn). Since Figure 11 indicates that the difference in efficiency using the two bases is reasonably constant over the thickness range tested and the efficiency based on excluding the ejected oil is more representative of larger burns (in which most of the ejected oil would fall back onto the burning slick), the basis for comparison of burn efficiency was selected to be that excluding ejected oil.

Figure 12 compares oil removal rates (or burn rates) for unemulsified oil calculated using the two bases. For the reasons given above, the burn rate excluding ejected oil was chosen for comparison.

Burn Efficiency

Figure 13 shows the effect of weathering and emulsification on oil removal efficiency as a function of slick thickness calculated on an oil only basis (i.e., $\text{efficiency} = 100\% \times (1 - \text{mass of oil remaining inside ring} / \text{mass of oil in emulsion placed in ring})$). In all tests involving successful ignition of the slick the residue remaining in the ring was composed of water-free oil.

For the case of the unemulsified oils (open symbols joined by a solid line) the degree of weathering had little effect on burn efficiency. Burn efficiencies increased from about 50% for 2 mm thick slicks to about 80% for 5 mm thick slicks to about 90% for 10 mm thick slicks, in accordance with other studies (Energetex 1976; S.L. Ross and Energetex 1985). The addition of 25% water emulsified with the oil (open

TABLE 2
In-Situ Ignition Success

Oil	% Evaporated	% Water	Smallest Thickness Ignited (mm)	5 cm square pad	Ignited By 10 cm square pad	2 mm fresh oil
C-96	0	0	2	Y		
		25	5	Y		
		50	>10	N	N	N
	5	0	2	Y		
		25	2	Y		
		50	5	N	N	Y
		75	>10	N	N	N
	10	0	2	Y		
		25	5	N	Y	
		50	>10	N	N	N
	B-27	0	2	Y		
		25	2	Y		
		50	5	Y		
		75	10	N	N	Y
	8	0	2	Y		
		25	5	Y		
		50	5	Y		
		75	10	N	Y	
	14	0	2	Y		
		25	2	Y		
		50	5	Y		
		75	10	N	N	Y



**Figure 7 – Droplets
being ejected from
unemulsified oil
near end of burn**



**Figure 8 – Droplets
being ejected
during emulsion
burn**

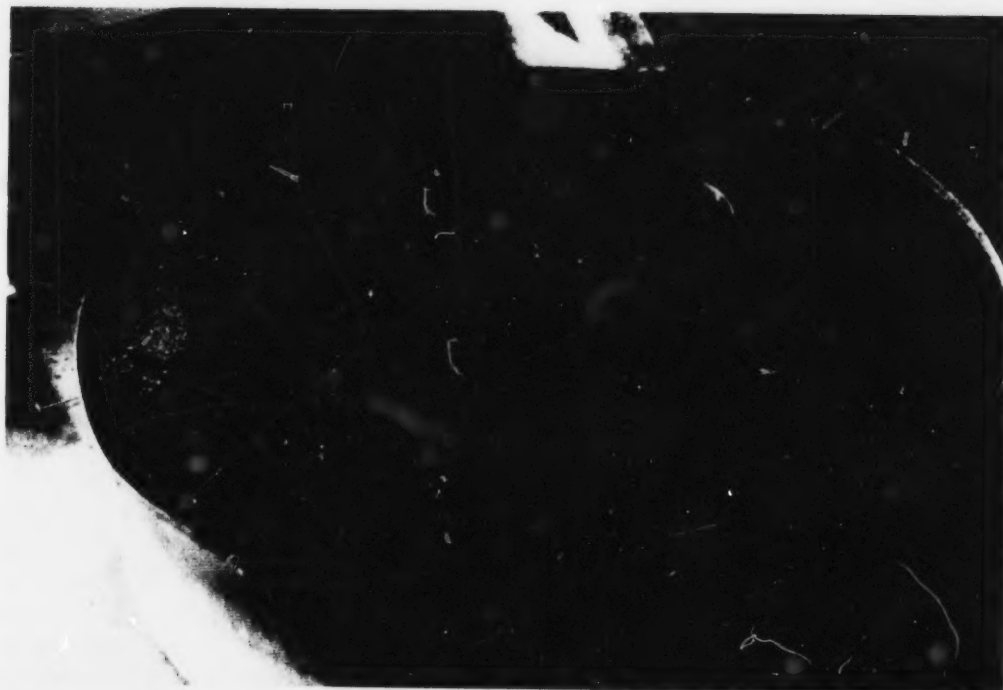
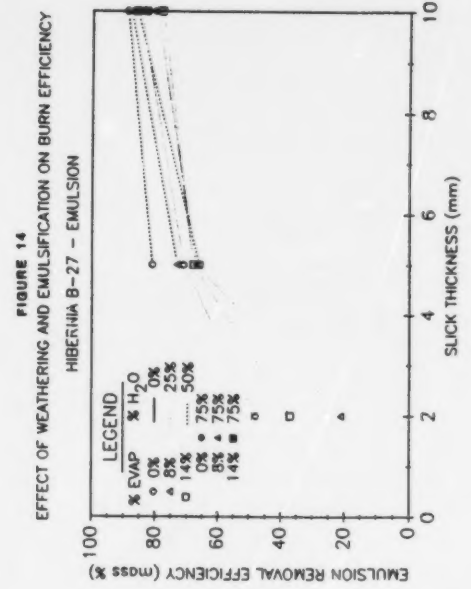
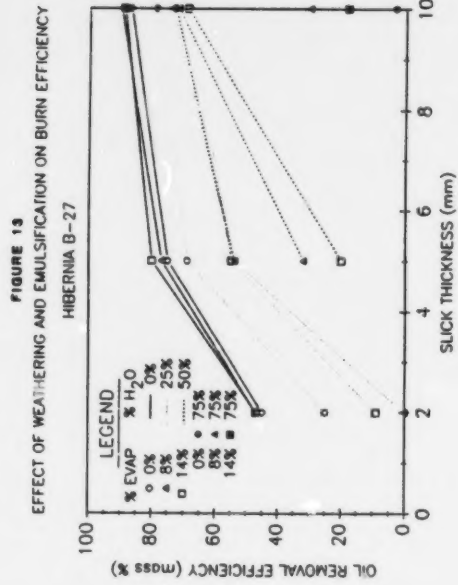
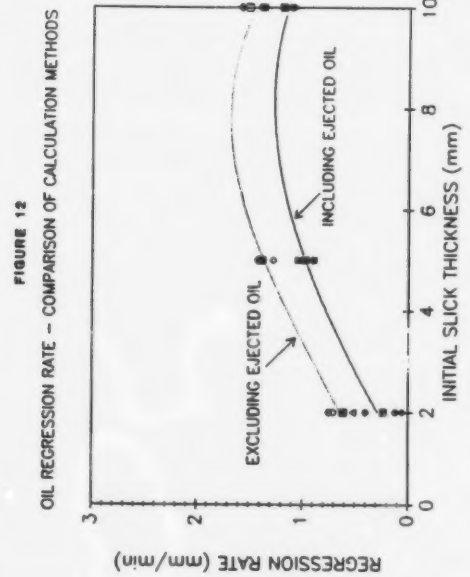
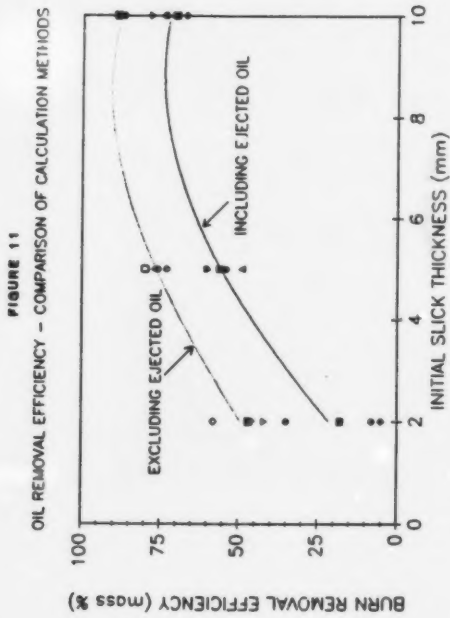


Figure 9 - Oil and emulsion ejected during in-situ burn of 50% water emulsion



Figure 10 - Oil ejected during in-situ burn of unemulsified oil



symbols joined by a dotted line) reduced oil removal efficiencies for the fresh oil by some 10% for the thicker slicks (20% for the 2 mm thick slick) and caused the effect of weathering to become more apparent. The weathered 25% water B-27 emulsions 5 and 10 mm thick showed a 15-25% decrease in oil removal efficiency compared with the unemulsified case. The 2 mm thick weathered 25% water B-27 emulsions had very low (0-10%) oil removal efficiencies. Increasing the water content to 50% further decreased the oil removal efficiency to about 50, 30 and 20% for 5 mm thick slicks of fresh, 8% and 14% weathered B-27 oil respectively but had little effect on the oil removal efficiencies for 10 mm thick slicks. The oil removal efficiencies for the 10 mm thick 75% water emulsions (solid symbols) were about: 5% for the fresh oil, 30% for the 8% weathered oil, and 20% for the 14% weathered oil.

Figure 14 shows the results for the emulsified slicks where the removal efficiency was calculated by: $\text{efficiency} = 100\% \times (1 - \text{mass of oil remaining in ring} / \text{mass of emulsion placed in ring})$. This represents the emulsion removal efficiency and includes emulsified water vaporized as well as oil burned from the test slick. In this case, emulsion water content had little effect on removal efficiency except for the 2 mm thick slicks. Emulsion removal efficiencies were in the 65-80% range for 5 mm thick slicks and in the 75-90% range for 10 mm thick slicks, even with 75% water emulsions.

Figure 15 compares the removal efficiency (either oil or emulsion) for 10 mm thick slicks of fresh and weathered B-27 crude as a function of emulsion water content. This shows more clearly the effects of burning emulsions. Regardless of water content up to 75% the emulsion removal efficiency is reasonably constant at 85-90%; however, the oil removal efficiency drops steadily up to 50% water then drops dramatically at 75% water. There are two reasons for this; first, although each slick is initially 10 mm thick, as the water content increases the equivalent thickness of oil decreases (i.e., a 75% water slick has only 2.5 mm of oil initially and thus the best possible efficiency would be $1 - 1 \text{ mm remaining} / 2.5 \text{ mm initially} = 60\%$); and second, more of the heat required to vaporize oil to sustain combustion is spent vaporizing water.

Figure 16 shows the effect of weathering and emulsification on the oil removal efficiency for C-96 crude as a function of slick thickness. As with the B-27 crude (see Figure 13) the addition of 25% water to the C-96 crude reduced the removal efficiency by about 10% for the thicker slicks; unlike the B-27 crude, the 2 mm thick slick was unignitable for the weathered oils. As well, the 50% water slicks burned very poorly, resulting in combustion only in the case of the 10 mm slicks with removal efficiencies of 30% for the 5% weathered C-96 emulsion and 5% for the 10% C-96 emulsion. The 10 mm thick, 5% weathered, 75% water slick had an oil removal efficiency of just greater than 0.

Figure 17 shows the emulsion removal efficiencies calculated for the same runs. The 2 mm thick slicks showed poor combustion efficiencies. Increasing the emulsion water content from 25 to 50% results in a decrease in emulsion removal efficiency of about 20% for the 5% weathered slicks with 5 and 10 mm thickness. None of the more weathered or more emulsified slicks could be ignited.

Figure 18 compares the removal efficiencies (oil or emulsion) for the 10 mm thick slicks of C-96 crude as a function of water content. In the case of this oil both the emulsion and oil removal efficiencies declined steadily as water contents approached and exceeded 50%. The emulsion removal efficiency also seemed to be a function of weathering for the C-96 oil, unlike that of the B-27 crude (see Figure 15).

FIGURE 17
EFFECT OF WEATHERING AND EMULSIFICATION ON BURN EFFICIENCY
HIBERNIA C-96 - EMULSION

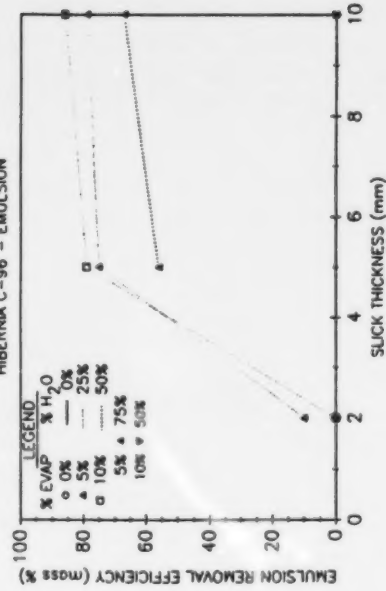


FIGURE 18
EFFECT OF EMULSIFICATION ON BURN EFFICIENCY
HIBERNIA B-27 - 10mm SLICK

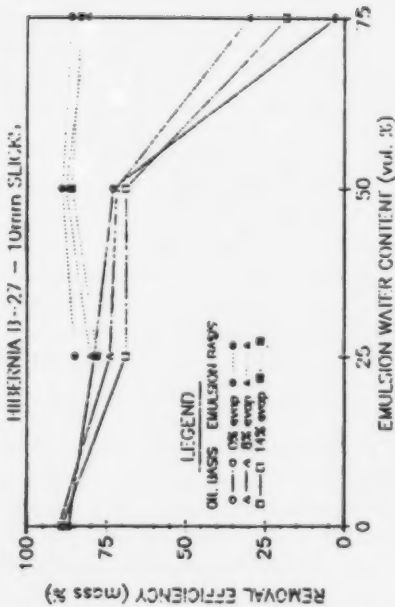


FIGURE 19
EFFECT OF EMULSIFICATION ON BURN EFFICIENCY
HIBERNIA C-96 - 10 mm SLICKS

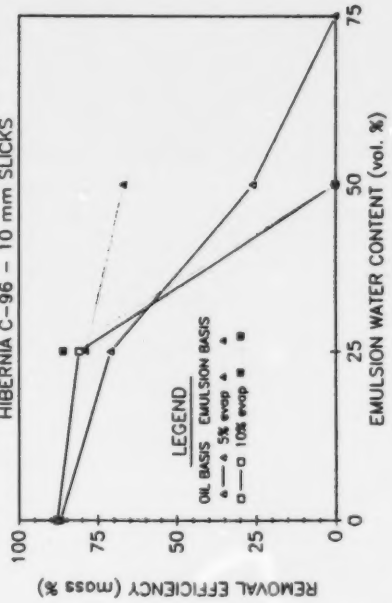
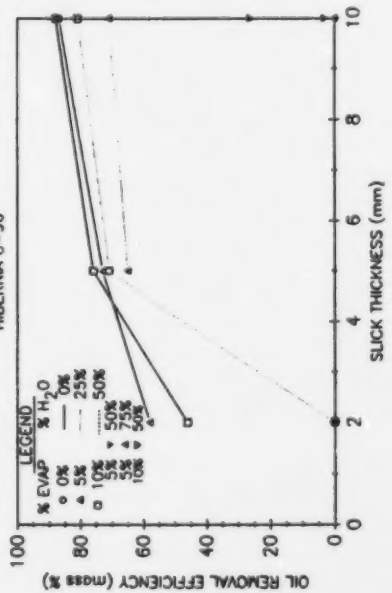


FIGURE 20
EFFECT OF WEATHERING AND EMULSIFICATION ON BURN EFFICIENCY
HIBERNIA C-96



This may be related to the higher pour point ("waxiness") of the C-96 oil in some unknown way.

Burn Rate

Figure 19 shows the effect of weathering and emulsification on oil burning rate (rate = oil burning efficiency x oil content of emulsion x initial thickness/burn time) as a function of slick thickness. The data for the unemulsified oils shows that burn rates increased from about 0.5 mm/min for 2 mm slicks to about 1.5 mm for 5 and 10 mm slicks; weathering had little effect on the burn rate.

The slicks of 25% water emulsion burned oil at a slower rate, between 0 and 0.24 mm/min for the 2 mm thick slicks, between 0.5 and 0.75 mm/min for the 5 mm thick slicks and between 1 and 1.25 mm/min for the 10 mm thick slicks. The higher values in each range were associated with fresh oil emulsions; weathering reduced burn rates slightly. In the case of emulsions of the B-27 oil containing 50% water oil burn rates were reduced further to 0.25 - 0.5 mm/min for 5 mm thick slicks and 0.5-0.75 mm/min for 10 mm thick slicks. At 75% water only two of the three 10 mm thick slicks tested could be ignited (fresh and 8% weathered oil) and had oil burn rates of only 0.02 and 0.1 mm/min respectively.

Figure 20 shows the emulsion removal rates (rate = emulsion burn efficiency x initial thickness/burn time) calculated for the same tests. In this case emulsion removal rates increased from 0.25 - 0.5 mm/min for 2 mm slicks to 1-1.25 mm/min for 5 mm slicks to 1.5-2.25 mm/min for 10 mm slicks. There was little discernible effect of weathering or water content on emulsion removal rate; if anything, increasing water content slightly increased emulsion removal rate.

Figure 21 compares the removal rates (oil and emulsion) for 10 mm thick slicks of B-27 crude as a function of emulsion water content. It is clear that as water contents increased oil removal rates decreased steadily and emulsion removal rates increased. With less oil per millimetre of slick, and more water to vaporize, the oil burned more slowly and gave up more of its energy to evaporating water.

Figure 22 shows the effects of weathering and emulsification on oil burning rates for the C-96 oil as a function of slick thickness. The burn rate of unemulsified C-96 crude was almost identical to that of unemulsified B-27 crude (see Figure 19). The addition of 25% water rendered the 2 mm thick slicks virtually unburnable and reduced the 5 mm and 10 mm burning rates to 0.5-0.75 mm/min. Of the more weathered, more emulsified slicks only the 5 mm thick slick with 50% water could be ignited and had an oil burning rate of about 0.2 mm/min.

Figure 23 shows the emulsion removal rates calculated for the same runs. The data for the C-96 crude exhibits the same trends as that for the B-27 crude. Increasing slick thickness increased emulsion removal rates and increasing water content increased emulsion removal rates.

Figure 24 better illustrates the effect of water content on removal rate (oil or emulsion) for 10 mm slicks of C-96 crude; as water contents increased, oil burning rates steadily decreased and, as water contents increased emulsion burning rates increased until the maximum burnable water content was reached (between 50 and 75% for 5% evaporated C-96 and between 25 and 50% for 10% evaporated C-96).

FIGURE 19
EFFECT OF WEATHERING AND EMULSIFICATION ON BURN RATE
HIBERNIA B-27

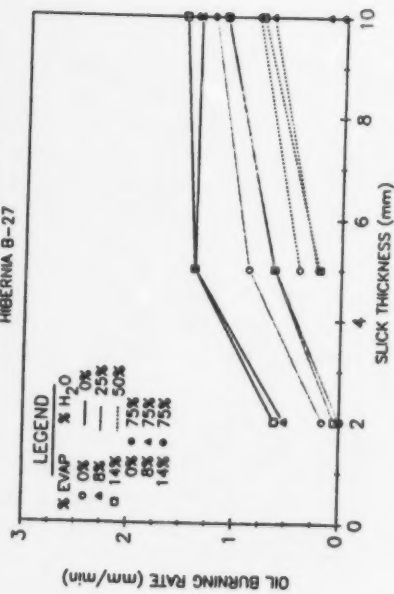


FIGURE 21
EFFECT OF EMULSIFICATION ON REMOVAL RATE
HIBERNIA B-27 - 10mm SLICKS

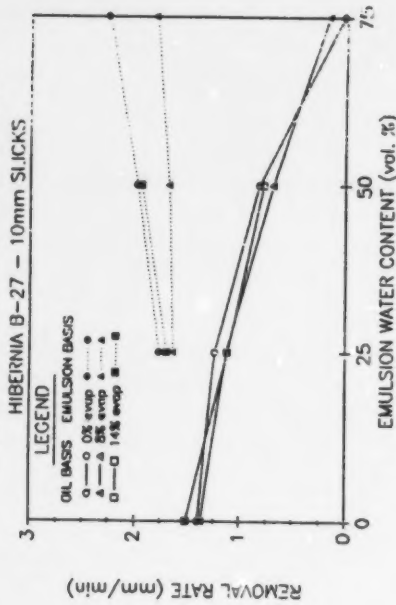


FIGURE 20
EFFECT OF WEATHERING AND EMULSIFICATION ON REMOVAL RATE
HIBERNIA B-27 - EMULSION

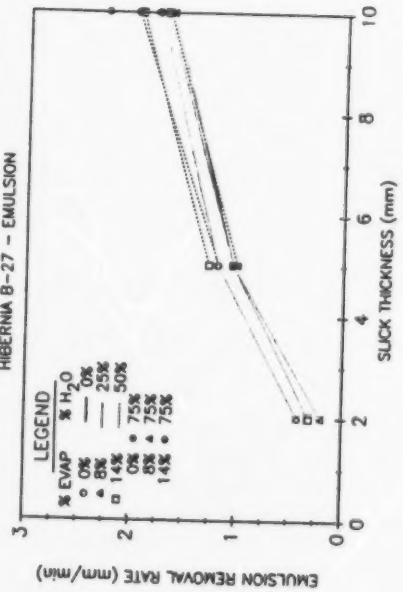


FIGURE 22
EFFECT OF WEATHERING AND EMULSIFICATION ON BURN RATE
HIBERNIA C-96

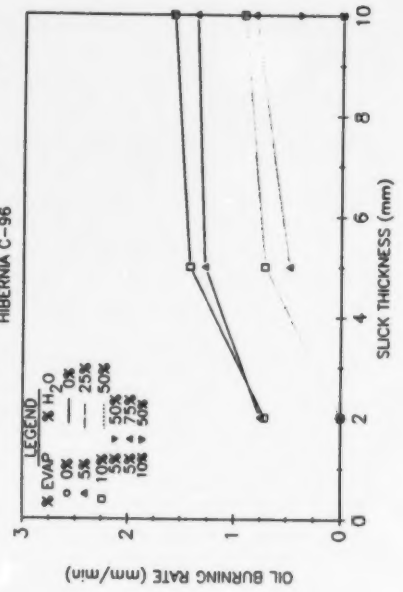


FIGURE 23

EFFECT OF WEATHERING AND EMULSIFICATION ON REMOVAL RATE

HIBERNIA C-96 - EMULSION

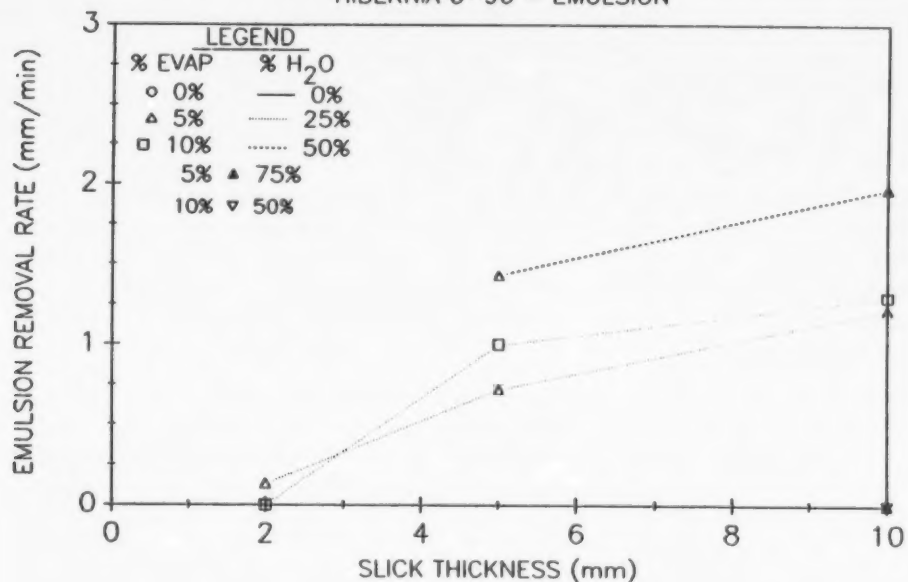
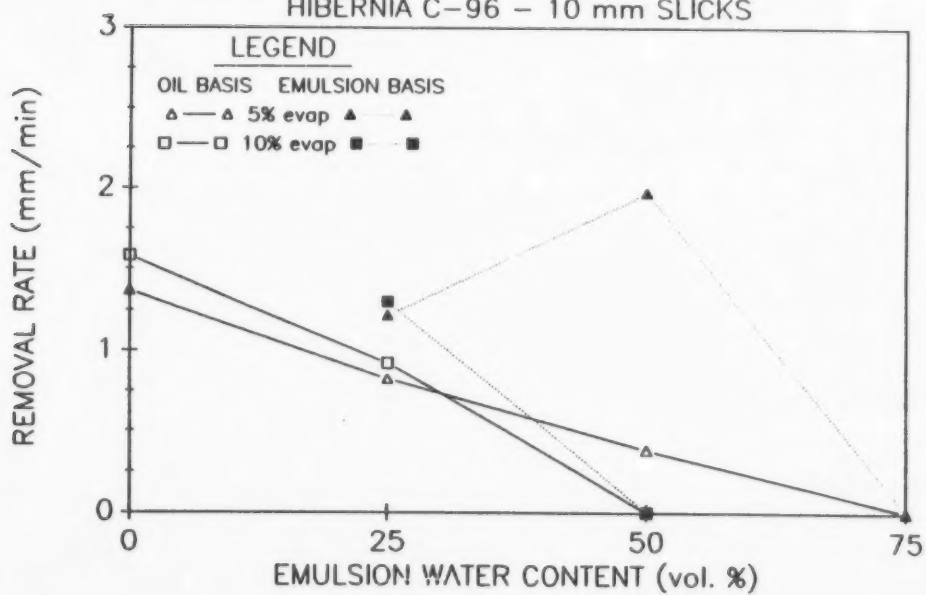


FIGURE 24

EFFECT OF EMULSIFICATION ON REMOVAL RATE

HIBERNIA C-96 - 10 mm SLICKS



DESIGN, FABRICATION AND TESTING OF THE "SWIRLFIRES" BURNER

EQUIPMENT AND METHODS

The "Swirlfire" Burner

A prototype "Swirlfire" burner was designed and constructed for this portion of the study. The device (Figures 25 and 26) is based on a design originally developed by Mr. Ed Twardus of Energetex Engineering and consists of a single unit incorporating a diesel engine, fan, rotary cup atomizer and combustion head. The prototype, designed to be heli-portable, incorporates pad-eyes for stable lifting and weighs about 400 kg dry.

The unique features of this burner, compared with other portable oil-spill disposal burners such as the Saacke system (Buist and Vanderkooy 1982) are: first, the "Swirlfire" delivers about 40–50% excess air (i.e., 140–150% of the stoichiometric air required for combustion); second, the "Swirlfire" burner utilizes two fuel atomization processes, the primary system being a rotary cup and the secondary system being impingement of oil on a hot steel plate inside the combustion chamber; and third, the combustion chamber itself incorporates a unique recirculation system and swirling motion to extend retention times and encourage complete, smokeless combustion.

A full parts list, operating instructions and maintenance instructions may be found in the report (S.L. Ross 1989).

Test Oils

Five oil types were used to test the capabilities of the burner, including: two crudes with various emulsion water contents, Bunker "C", diesel and waste engine oil. The properties of the fresh, unemulsified oils are given in Table 3. Emulsions for the tests were prepared by mixing appropriate volumes of crude oil and tap water in a 22.7 L pail with a high-speed mixer. Properties of the emulsions of the crudes were not measured.

TABLE 3

Physical Properties of Fresh Oils for the "Swirlfire" Tests

Oil	Density (kg/m ³) @ 10°C	Viscosity (mPas) @ 10°C	Pour Point	Flash Point
HIBERNIA B-27	878	240	9	11
UVILUK P-66	900	15	N.M.*	N.M.
DIESEL	831	2.9	-20 ⁺	55 ⁺
BUNKER "C"	1018	111,000	5 ⁺	>110 ⁺
WASTE ENGINE OIL	880 ⁺	200 ⁺	-36 ⁺	190 ⁺

* not measured

+ from Bobra 1989

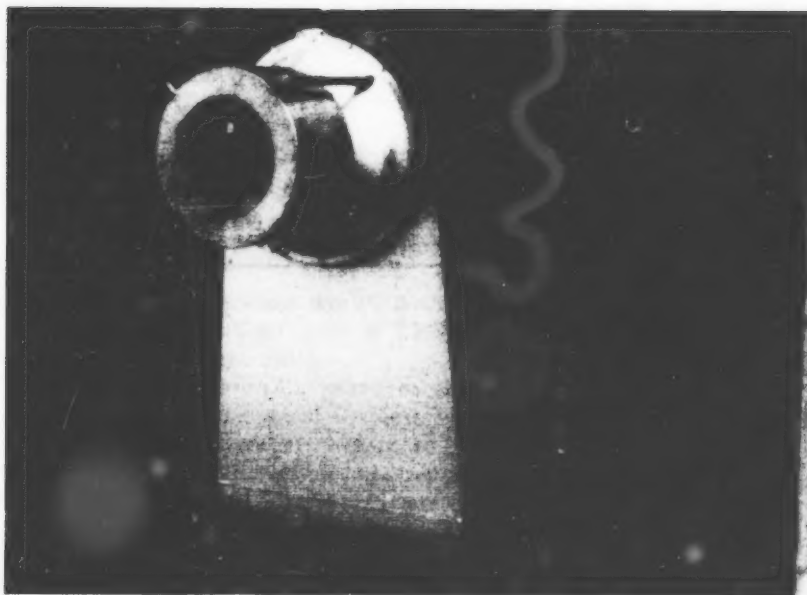
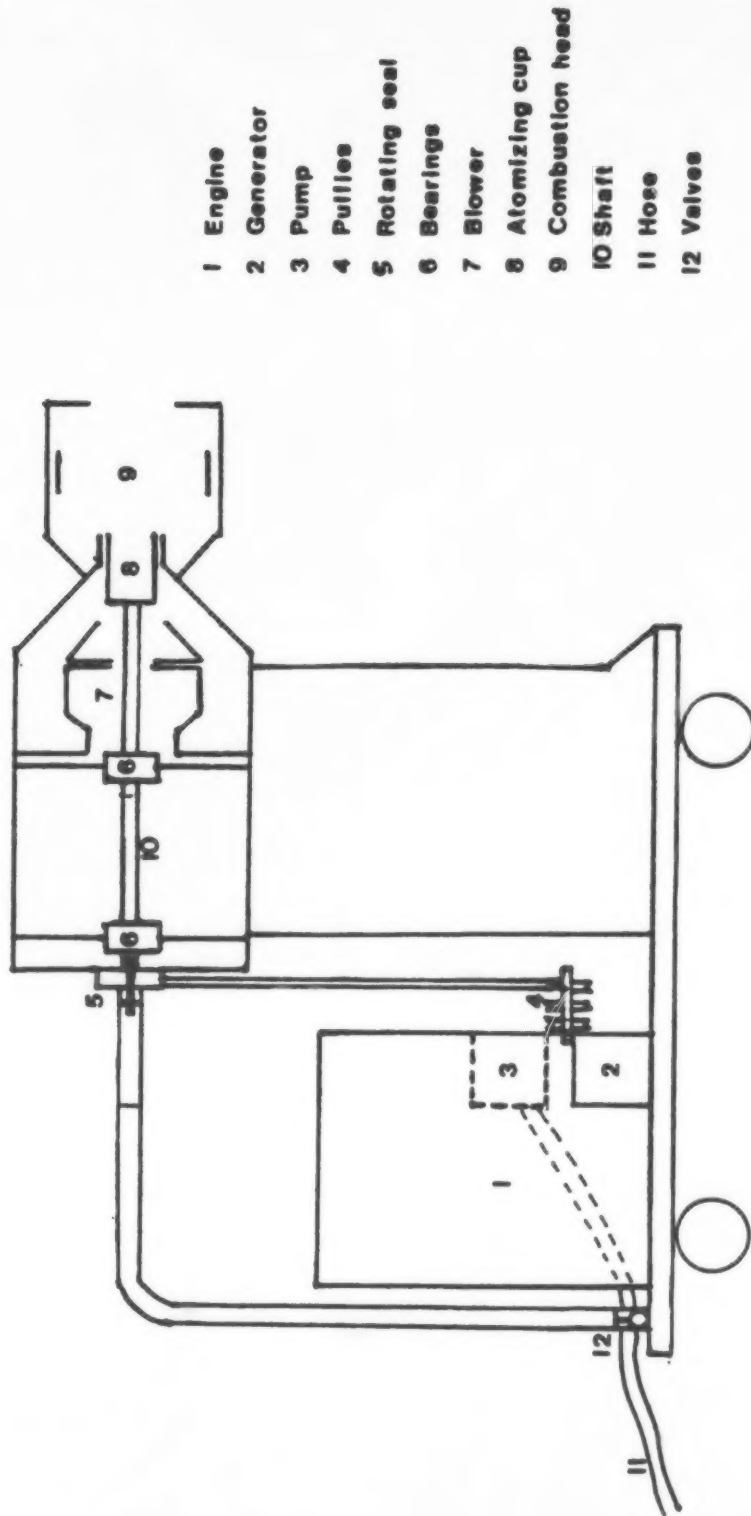


Figure 25 — The prototype "Swirlfire" burner showing the combustion chamber, rotary cup and ignition port

FIGURE 26
Schematic of the "Swirlfire" Burner



Test Measurements

The following were recorded during each test:

- * oil or emulsion flowrate (by timing the decrease in height of oil in a 22.7 L pail from which the oil or emulsion was pumped)
- * engine speed (rpm from a tachometer; fan and cup rpm = $1.54 \times$ engine rpm; pump rpm = $0.5 \times$ engine rpm)
- * pump discharge pressure
- * flame emissions (soot and fallout visually)

Following the test series, the burner was connected to a section of ducting and the airflow generated by the fan at various speeds was determined by measuring air velocity profiles in the duct (see the report).

Test Procedures

The following procedures were followed for each test:

1. the engine was started and run up to 700–800 rpm;
2. the pump suction hose was placed in a jerrycan of diesel fuel;
3. the shutoff valve was opened and the flow control valve opened one turn;
4. when diesel began to be atomized by the rotary cup, a burning, diesel-coated rag secured around the end of a steel bar was inserted into the ignition port and placed at the bottom of the combustion chamber; the diesel ignited in about 1 minute;
5. the burner was allowed to warm up for 3–5 minutes burning diesel;
6. the suction hose was moved into a 22.7 L pail of the test oil or emulsion and the oil or emulsion level recorded;
7. the height of oil or emulsion was recorded periodically, after each measurement the flow control valve was opened further;
8. once the combustion chamber began to produce smoke, the flow control valve was reduced $\frac{1}{2}$ turn and the suction hose replaced in diesel fuel;
9. the burner was run until diesel reached the rotary cup, then the shutoff valve was closed the burner allowed to extinguish and cool down.

RESULTS AND DISCUSSION

Table 4 shows the highest flowrates of oil or emulsion recorded for the various test oils that resulted in a smokeless burn. Complete data for each test may be found in the report (S.L. Ross 1989). The results for unemulsified oil ranged from 0.76 L/min (6.9 bbl/day) for Bunker "C" to 1.88 L/min (17 bbl/day) for diesel oil; the crude oils were burned cleanly at rates in the 1.32–1.46 L/min range (12–13 bbl/day) and the waste engine oil was burned at 1.19 L/min (10.8 bbl/day). On the basis of the combustion rates for the unemulsified crudes and the diesel fuel and accounting for the different operating speeds, the nominal capacity of the prototype, for clean combustion, is in the 1.6 L/min (14 bbl/day = 21 gal/hr) range.

TABLE 4

Maximum Clean Combustion Rate Results

Oil	% Water (Volume)	Engine RPM	Pump Pressure (kPa)	Max. Combustion Rate (L/min)	(bbl/day)	Comments
Hibernia B-27	0	1400	165	1.32	12.0	clean burn
	25	1500	165	2.08	18.8	clean burn; some droplet fallout
	50	1600	165	2.71	24.5	clean burn; some droplet fallout
	66	1600	150	4.19	37.9	very clean burn; droplet fallout; max. pump rate
Weathered UVILUK P-66	0	1600	150	1.46	13.2	clean burn
	25	1600	150	2.96	26.8	clean burn
Bunker "C" (preheated to 49°C)	0	1600	170	0.76	6.9	some light smoke
waste engine oil	0	1600	150	1.19	10.8	clean burn
diesel	0	1700	150	1.88	17.0	very light smoke

When burning unemulsified crude oil the combustion process was very clean (Figures 27 and 28) with the flame at the maximum rate extending only some 30–40 cm out of the combustion chamber. If the flowrate was increased above the maximum clean burn rate the flames extended farther and some smoke was generated (Figure 29). Burning diesel fuel produced a very clean flame (Figure 30) at rates below the maximum as did the combustion of the waste engine oil (Figure 31). Burning Bunker "C" produced some light smoke regardless of flowrate (Figure 32) and some carbon residue was found inside the combustion chamber after the test (Figure 33).

As the water content of the crude oil emulsions increased the maximum clean burn rate increased. As shown in Figure 34, the increase in maximum clean burn rate was inversely proportional to the fraction of water in the fuel up to 66% water (the highest tested). As the water content increased, the characteristics of the flame changed as well. With 25% water in the crude oil the flame was slightly less luminous (Figure 35) than the water-free oil test (Figure 27) and slightly longer (about 50 cm vs. 30–40 cm). Some small water drops were ejected from the burner at the maximum combustion rate with the 25% water-in-oil emulsion.

At 50% water content, the flame was considerably less luminous than at 25% water (Figure 36) and slightly longer again (70 cm vs. 50 cm). Some small water drops were ejected from the combustion chamber during this test and, after the test, it was noted that some water had pooled in the bottom of the chamber (a drain plug is provided for its removal).

At 66% water content, the flame was almost invisible (Figure 37) and droplets of water, containing a small amount of oil, were observed to be ejected from the lower lip of the combustion chamber. After the test a considerable volume of water with a small amount of oil floating on top was discovered in the bottom of the chamber. Consideration should be given to providing a tube running from the drain in the chamber to allow continuous draining of this accumulated water. This tube could perhaps run back to a container where the oil could be separated and recycled into the burner.

During the tests with emulsions the efficacy of the secondary atomization system (the hot steel plate mounted inside the circumference of the chamber) became clear. It was obvious that a considerable fraction of the atomization was taking place at this plate; without it it seems unlikely that the high-water-content emulsions could have been successfully burned.

It should be noted that in one test (50% water content emulsion of weathered Uviluk P-66 crude oil) the emulsion separated and the pump sucked water which instantly extinguished the flames. Reignition required purging the lines with diesel and relighting the burner – a process that took about 5 minutes.

RECOMMENDED MODIFICATIONS TO THE PROTOTYPE

Although the prototype "Swirlfire" burner performed admirably during the tests, several modifications are required for more efficient use of such a device in field situations; many of these are very minor. They are listed in the report (S.L. Ross 1989).



Figure 27 — Burning unemulsified Hibernia B-27 crude oil

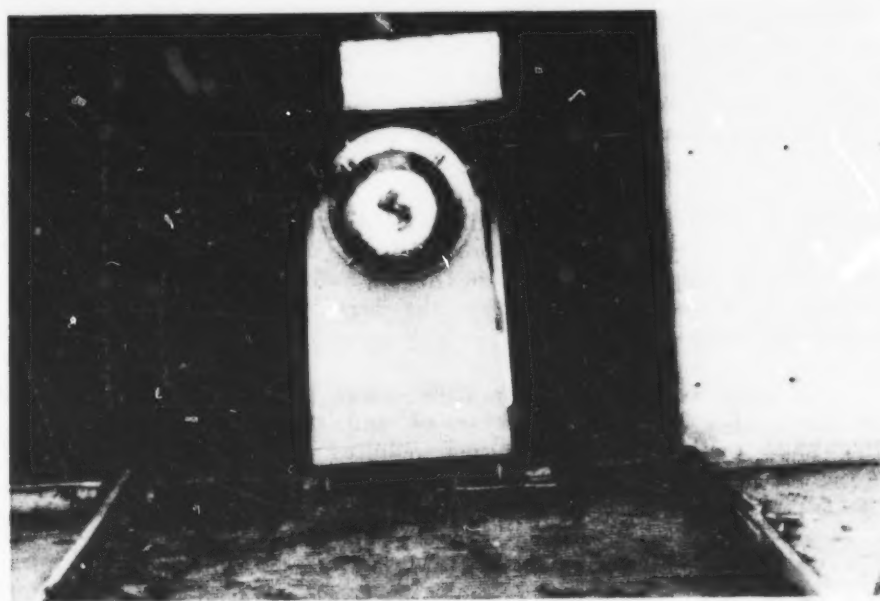


Figure 28 — As above; note swirling action of flame in combustion chamber



Figure 29 - Smoke generated when burning crude oil at rate above maximum clean rate



Figure 30 - Clean burn of diesel fuel

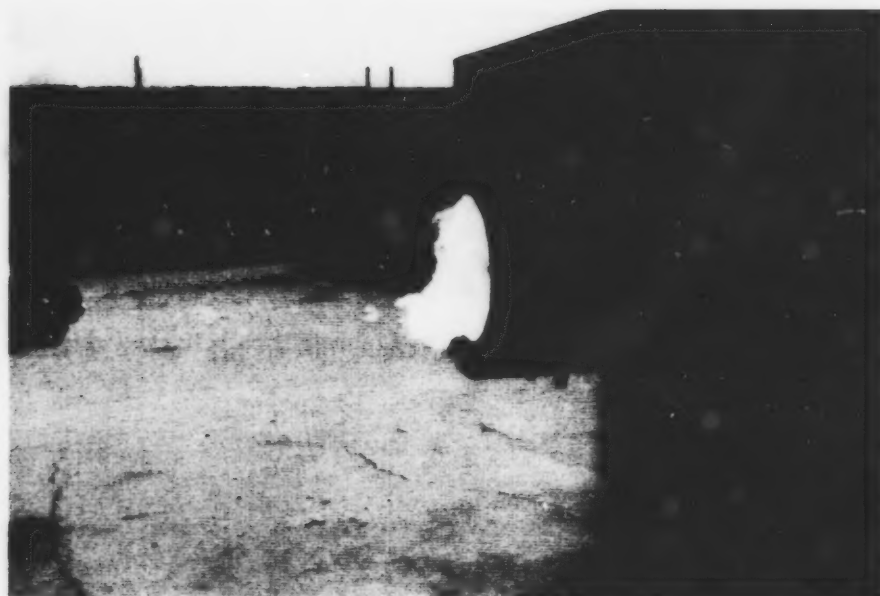


Figure 31 -- Clean burn of waste engine oil



Figure 32 — Smoke generated when burning Bunker "C"



Figure 33 — Residue remaining inside combustion chamber after Bunker "C" burn

FIGURE 34
EFFECT OF EMULSION WATER CONTENT ON
MAXIMUM CLEAN COMBUSTION RATE OF THE "SWIRLFIRE"

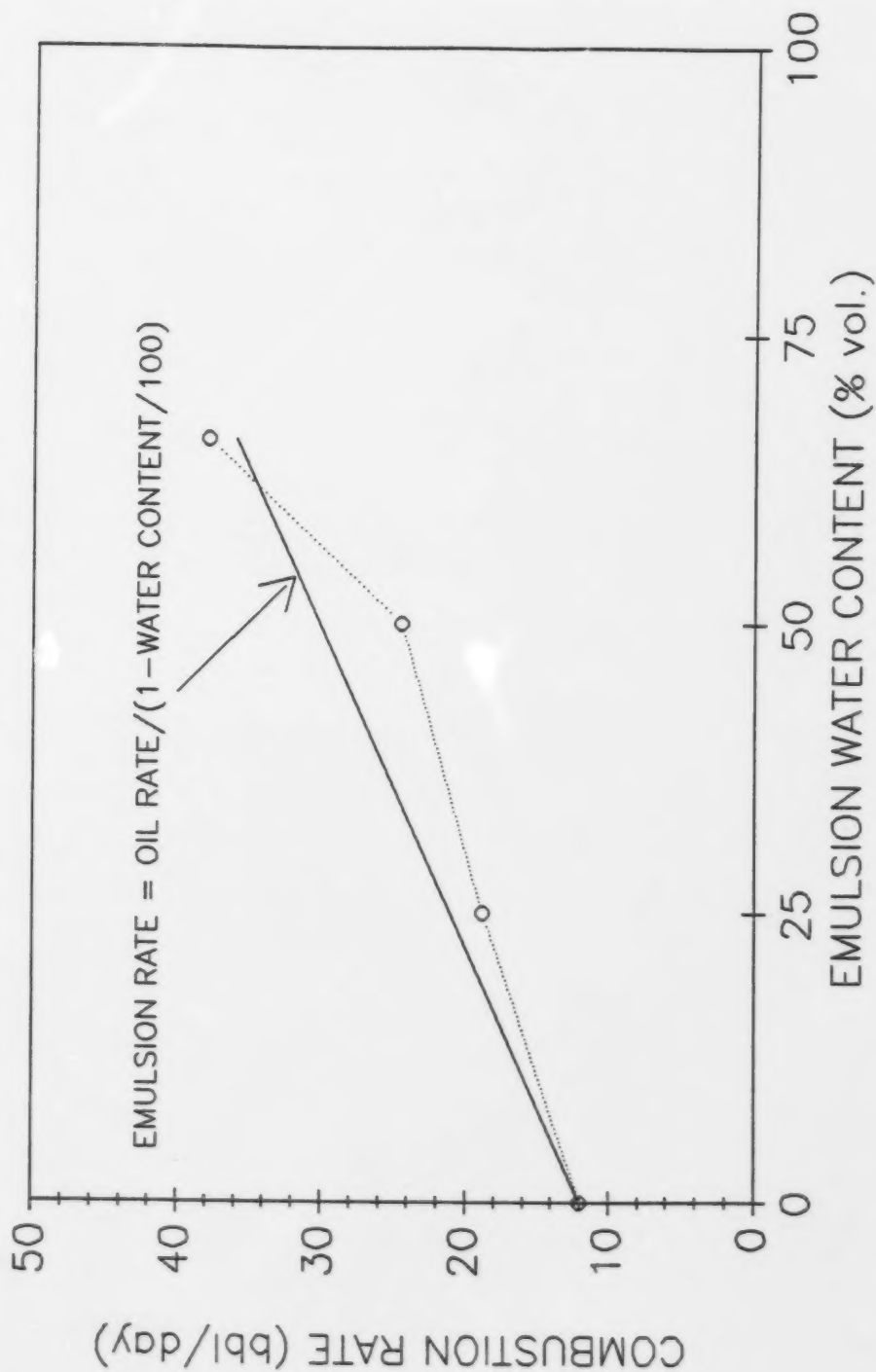




Figure 35 - Appearance of flame when burning 25% water-in-Hibernia B-27 emulsion

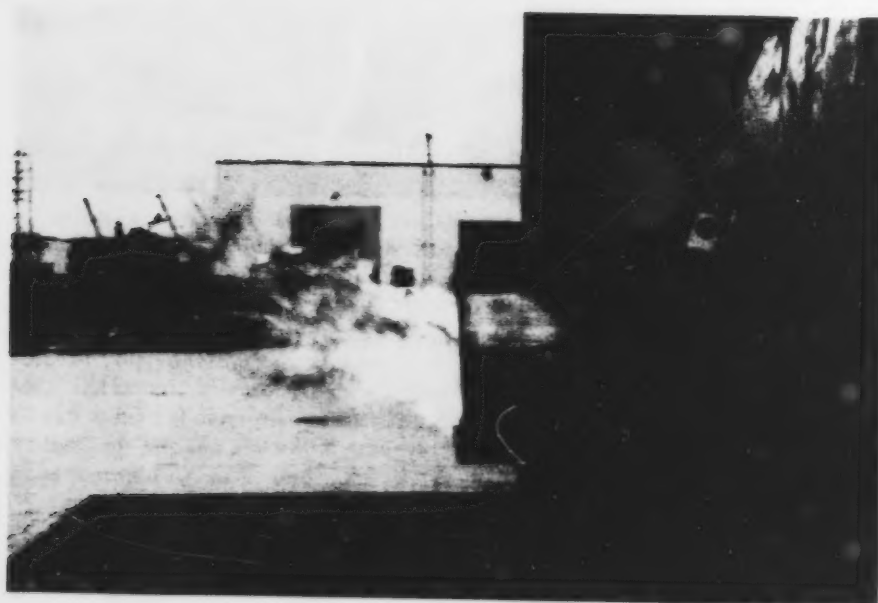


Figure 36 Appearance of flame when burning 50% water-in-oil Hibernia B-27



**Figure 37 — Appearance of flame when burning 66% water-in-Hibernia B-27 emulsion;
note droplets coming from lower lip of combustion chamber**

As well as these minor modifications, based on experience with the prototype, the following are recommended:

- * the maximum capacity of the prototype (i.e., ignoring smoke generation) should be determined in an open area;
- * a longer (several hours) burn should be undertaken with emulsified oil to determine any effects of long-term use; and
- * a larger capacity device (10 times the capacity of the prototype would provide a capability to dispose of $16 \text{ L/min} = 145 \text{ bbl/day} = 210 \text{ gal/hr}$ as recommended in a previous study on oily waste disposal (S.L. Ross 1988)) should be designed, constructed and tested. Rough calculations indicate that this may be possible with less than a doubling of the weight of the unit.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In-Situ Burning of Hibernia Crude Oil Spills

1. emulsions of the Hibernia C-96 crude proved to be more difficult to ignite and burn than those of the Hibernia B-27 crude;
2. the ignition times of slicks increased slightly with increasing weathering and increased dramatically with emulsification; flames would not spread over most slicks with water contents in excess of 50%;
3. the results of ignition tests with oil-soaked sorbent pad squares indicate that thick ($>2 \text{ mm}$) slicks of oil should be easily ignitable with a "Helitorch" well beyond 12 hrs after a spill occurs; thick ($>2-5 \text{ mm}$) slicks of emulsion should be ignitable by a Helitorch for up to about 12 hours after a spill occurs providing the emulsion water content is in or below the 25-50% range for Hibernia C-96 crude and in or below the 50% range for Hibernia B-27 crude;
4. slicks of emulsion with water contents in excess of these maximums can be ignited using a layer of fresh oil to initiate combustion over a larger slick area than can be achieved with the "Helitorch"; the maximum ignitable water content for thick (10 mm) slicks of emulsion using this technique was 50% for the Hibernia C-96 crude and 75% for the Hibernia B-27 crude;
5. oil burning efficiency increases with increased slick thickness, is not a strong function of oil weathering and decreases with increasing emulsification. Thick (10 mm) slicks of unemulsified oil had burn efficiencies in the 85-90% range. Thick (10 mm) slicks of emulsified oil containing 25% water had oil burn efficiencies of in the 70-80% range. Thick (10 mm) slicks of Hibernia B-27 emulsions containing 50% and 75% water had burn efficiencies in the 70-75% and 5-35% range respectively. Thick (10 mm) slicks of Hibernia C-96 emulsion with water contents of 50% and greater were generally unignitable;
6. emulsion removal efficiency (including both oil burned and water evaporated) increased with increasing water content up to the point where the slick was no longer ignitable. This, combined with the dramatic reduction in oil burning efficiency with increasing water content over 50% implies that, in the event of a real spill, two ignitions may be required: the first would be used to vaporize most of the water from the slick; after herding the residue to thicken it, the second would be used to burn off the oil; and

7. increasing water content of an emulsion from zero to the maximum ignitable, reduces the oil burning rate but increases the emulsion removal rate.

Testing of the "Swirlfire" Burner

1. The "Swirlfire" burner successfully combusted water-free crude oil at rates of 1.32–1.46 L/min (12–13 bbl/day) with no smoke;
2. Water-in-crude oil emulsions were burned cleanly up to a maximum 66% water content (the highest tested);
3. The rate at which the device could burn water-in-oil emulsions cleanly was inversely proportional to the fraction of oil in the emulsion (i.e., a 66% water content emulsion burned at a rate about 3 times that of the clean burn rate of the parent oil);
4. Diesel fuel and waste engine oil were burned cleanly at rates of 1.88 and 1.19 L/min (17 and 10.8 bbl/day) respectively;
5. Bunker "C" preheated to 50°C, was burned at a rate of 0.76 L/min (6.9 bbl/day); some smoke was generated regardless of flowrate.

RECOMMENDATIONS

In-Situ Burning of Hibernia Crude Oil Spills

1. The potential for rapid, efficient removal of oil spills by in-situ burning warrants that field trials of the technique be carried out offshore to assess "real world" ignitability, removal rates and removal efficiencies in wave conditions for slicks both contained by fireproof booms and uncontained.
2. The purchase, for field testing, of a "Helitorch" aerial ignition system is recommended.

Testing of the "Swirlfire" Burner

1. A number of minor modifications to the prototype are suggested to improve its operational use. These are listed in the report.
2. Further testing of the prototype is recommended to evaluate its capability for long-term operation and determine its maximum achievable combustion rate, regardless of smoke generation.
3. A model of the "Swirlfire" with 10 times the nominal capacity of the existing prototype (i.e., 16 L/min = 145 bbl/day = 210 gal/hr) should be constructed and tested as an operational unit, providing the testing recommended above is satisfactory.

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A MODEL FOR EXPOSURE AND TOXICOLOGICAL IMPACT ASSESSMENT OF AROMATIC HYDROCARBON SPILLS IN THE AQUATIC ENVIRONMENT

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INTRODUCTION

Spills can be defined as sporadic or periodic discharges of unusually large amounts of a single or a mixture of substances in the environment. When detected, they often raise questions regarding their impact on the local environment and remedial actions required to alleviate environmental stress. The effect of the spill on biota is often of particular concern. A crucial part of any environmental impact assessment is therefore to determine or estimate (i) how much of the spilled substance(s) has been absorbed by organisms of the impacted ecosystem, (ii) to what extent the spilled substance can be transferred through the food-chain, and (iii) what are the (toxic) effects throughout the food-chain. To perform this component of an environmental impact assessment knowledge is required of (i) the distribution of the spilled substance(s) in the local environment, (ii) the exposure, including uptake, depuration, bioaccumulation and food-chain transfer, of the substance to biota, and (iii) the toxicity of the substance.

This paper reports a computer model ECOTOX, which describes the uptake, depuration and bioaccumulation of organic substances in various aquatic organisms such as algae, benthic invertebrates and fish. It also describes food-chain transfer and it can make predictions of toxic effects resulting from chemical exposure. The model is based on extensive research of chemical dynamics and toxicity in aquatic organisms. It can be used to estimate the response of the ecosystem to chemical exposure, resulting from chronic discharges or spills, in terms of exposure and toxicity. The ECOTOX model will be discussed and its practical application will be illustrated.

MODEL DEVELOPMENT AND PHILOSOPHY

ECOTOX is a computer model which predicts the body burden of organic chemicals in different compartments of the aquatic food-chain and resulting acute and chronic toxic effects (for some chemical classes) based on time-dependent input information of chemical concentrations in water and sediments. The model is dynamic i.e. it does not rely on steady-state or equilibrium

assumptions. This makes it particularly useful for spill events, which are characterized by unusual changes in environmental conditions.

The model incorporates equations for chemical uptake and elimination in fish, algae and benthic invertebrates. These equations have been tested in the laboratory and, in some cases, in the field. The entire model, combining all individually validated submodels of chemical uptake and depuration can be shown to fit field data reported by Oliver and Niimi (1988) on chemical concentrations in Lake Ontario organisms satisfactorily (unpublished). The model has not been validated for typical spill conditions. This may be difficult since it would require the control of a large number of variables. To avoid the difficulties associated with the validation of ecosystem response models such as ECOTOX, individual components of the model rather than the entire model are experimentally tested.

The model involves the following variables: K_{ow} of the chemical, the body weight, lipid content, growth rate, feeding rate, tropho-dynamics (i.e. predator-prey relationships), temperature, oxygen content of the water, concentration organic matter in the water, organic carbon fraction of the sediment. If available, knowledge of these variables and their variation with time can be simple incorporated in the model. If not available, ECOTOX will assume typical values for most (but not all, e.g. K_{ow}) of the variables. It is obvious that with more specific knowledge of the local environmental conditions and the biology of the ecosystem predictions of chemical body burdens and toxic effects can be more reliable. The model is therefore designed to be flexible in its input requirements such that bits and pieces of relevant information can be incorporated in the model when they are available.

The model is particularly useful for the assessment of the effects of a spill on an organism (e.g. a fish species) which is of particular ecological or economic importance. With specific information regarding the physiological and ecological characteristics of this organism ECOTOX is believed to give accurate predictions of chemical concentrations in aquatic organisms.

Since ECOTOX is a model for organic chemical dynamics and toxicity in aquatic organisms it is best combined with an environmental fate model (e.g. WASTOX). This provides a method to perform a complete environmental impact assessment on a ecosystem level.

MODEL LAY-OUT

It has been well documented that most aquatic organisms, such as algae, zooplankton, benthic invertebrates and fish are able to absorb organic chemicals directly from the water, predominantly via their respiratory surface (e.g. gills). This process is largely due to the ability of lipid phases in the organism to extract hydrophobic organic chemicals from the water. This process also allows the organism to depurate the chemical via the respiratory surface when the chemical concentration in the water drops. Alternatively, aquatic organisms absorb chemicals by consuming contaminated food. Food consumption can also provide a route of chemical depuration if the food is uncontaminated. In addition to chemical elimination to the water and to egested "faecal" phases metabolic transformation of the absorbed chemical is a route for chemical depuration. The chemical body burden in the organism is generally considered to be the result of the balance between the chemical uptake rates from water and food and the rate of chemical clearance. This can be mathematically expressed by the following differential equation, which describes simultaneous chemical uptake from food and water in aquatic organisms and depuration to the water (via the gills), into the faeces and by metabolic transformation:

$$dC_F/dt = k_1 \cdot C_W - k_2 \cdot C_F + k_A \cdot C_A - k_E \cdot C_F - k_R \cdot C_F \quad (1)$$

where C is concentration (mol/m^3), t is time (h), and the subscripts W refer to water, A to food, E to faeces, and F to the whole organism (Gobas et al. 1988, 1989). k_1 , k_2 , k_A and k_E are respectively the first order rate constants (h^{-1}) of chemical uptake from the water, elimination to the water, uptake from food, and elimination by egestion in faecal matter. k_R is the rate constant (h^{-1}) for metabolic transformation of the chemical in the organism.

Equation 1 treats all aquatic organisms as single homogeneous phases i.e. all the chemical within the organism is equally accessible. Equation 1 further assumes that chemical transfer processes in the organism are passive in nature, and that chemical concentrations in water, food and organism are too low for Michaelis-Menten kinetics to occur. Experiments involving organic chemicals and different organisms have demonstrated that the inherent assumptions of this organism-uptake model are generally applicable (Bruggeman 1982, Geyer et al. 1984, Spacie and Hamelink 1982).

Because the nature of chemical uptake and elimination routes in aquatic organisms tends to be the same (i.e. most organisms extract water for oxygen and consume food) equation 1 can be used to describe the uptake, elimination and bioaccumulation of organic substances in various aquatic organisms. The rate constants k_1 , k_2 , k_A and k_E , however, vary from organism to organism, and they are further dependent on the properties of the

chemical, the physiological condition of the organism and the ambient environmental conditions such as temperature and oxygen content of the water. For every combination of chemical, organism and environmental conditions there is a unique form of equation 1 with characteristic values for the rate constants. In order to develop methods to estimate the body burden of the organism resulting from environmental concentrations of a substance it is crucial to establish the rate constants of chemical uptake and depuration.

To derive the actual relationship between, for example, the water concentration of the spilled substance and the body burden of the affected organism equation 1 needs to be integrated. This can easily be achieved if (i) the water and food concentrations are constant, (ii) the body weight or volume of the organism is constant and (iii) the rate constants of chemical uptake and elimination do not vary with time. Neither of these conditions apply under typical spill conditions, which are characterized by large changes in local environmental concentrations. In addition, body weights of organisms vary with time as a result of natural cycles of feeding and starvation and they may also be affected by the spill itself. Rate constants of chemical uptake and elimination also vary with time, for example, due to natural or spill induced variations in environmental conditions such as water temperature, oxygen content or changes in feeding rates. It thus transpires that due to time dependent changes in virtually all variables integration of equation 1 is unfeasible. An alternative solution to integration is assuming steady-state (i.e. $dC_f/dt = 0$) conditions. This results in direct relationships between the concentrations in the organism, water and food sources, which are independent of time. Only when the response of chemical dynamics between the organism and the environment is more rapid than the change in condition causing the response (i.e. the organism is reacting to changes in environmental conditions virtually immediately) steady-state assumptions are appropriate. It has been shown that, in particular, higher K_{ow} chemicals (i.e. larger than 10^5) tend to require a very long time to reach steady-state levels in fish. In some cases the time to reach steady-state is comparable to the average life-time of the fish, thus indicating that the steady-state assumption is not applicable. If steady-state assumptions do not apply, such as for fish, ECOTOX performs a numerical integrations to derive the chemical concentration in the organism. The numerical integration involves the summation of increments in the organism concentration, dC_f , over time periods dt , which are calculated as

$$dC_f = (k_1 \cdot C_w - k_2 \cdot C_f + k_A \cdot C_A - k_E \cdot C_f - k_R \cdot C_f) \cdot dt \quad (2)$$

with C_f being dC_f .

ECOTOX incorporates equations for the chemical dynamics in (i)

algae and zooplankton, (ii) benthic invertebrates and (iii) four fish species of different trophic levels. These equations will now be briefly summarized.

Chemical Dynamics in Algae & Zooplankton

Laboratory experiments with Chlorella fusca and Selenastrum capricornutum demonstrate that uptake of organic chemicals from and elimination to the water are rapid with typical half-life times of 0.1 to 2 hours, corresponding to elimination rate constants of 6.9 to 0.3 h^{-1} (Mailhot 1987, Geyer et al. 1984, Wang et al. 1982). Although some algae species have been observed to feed on bacteria (Bird and Kalff, 1986) measurements of dietary chemical uptake rates have never been reported. Observation regarding chemical elimination to "faecal" phases and metabolic transformation of organic substances have also not been reported. Assuming that chemical uptake from food sources and chemical depuration by egestion in faecal matter and by metabolic transformation are insignificant equation 1 can be simplified to

$$dC_f/dt = k_1 \cdot C_w - k_2 \cdot C_f \quad (3)$$

Due to their short biological half-life times (or high depuration rate constants) algae are able to respond quickly to changes in environmental concentrations. It thus transpires that unless time frames associated with changes in environmental concentrations are shorter or comparable to those of the chemical dynamics in algae, algae and water are virtually at steady-state. This simplifies equation 3 to

$$C_f/C_w = k_1/k_2 \quad (4)$$

Experiments by Geyer et al. (1984) demonstrated that algae/water concentration ratios of chemicals at steady-state can be expressed as a function of the 1-octanol-water partition coefficient of the chemical, i.e.

$$C_f/C_w = L_A \cdot K_{OW} \quad (5)$$

where L_A is the lipid content of the algae species, which is typically between 0.005 and 0.02 depending on the species of interest. ECOTOX uses equation 5 to derive the body burden of algae as a function of the water concentration. The steady-state model for chemical dynamics in algae and zooplankton (i.e. equation 5) is believed to give accurate predictions unless chemical concentrations change very rapidly (e.g. doubling in concentration in minutes).

Chemical Dynamics in Fish

Bioaccumulation studies have demonstrated that equation 1 often gives a satisfactory description of the chemical dynamics in fish

(McKim et al. 1986, Gobas et al. 1989). The rate constants have been shown to be controlled by a variety of biological, chemical and environmental factors. This will be briefly summarized since ECOTOX incorporates various empirical, but mechanistically based, relationships between the body burden in fish and biological, chemical and environmental variables.

k_1 & k_2 : Gobas and Mackay (1987), Gobas et al. (1986) and Mackay and Hughes (1984) derived lipid-water mass transfer models to gain further insight into the processes controlling the exchange of chemical between aquatic organisms and water and to develop practical procedures to estimate the bioconcentration kinetics of chemicals in fish. The main feature of this model is that it views the exchange of solute chemical between the water and the organism to take place in a series of aqueous and lipid phases. All transport processes in water phases are therefore grouped together in one overall water phase transport parameter D_w . This overall water phase transport parameter contains all transport parameters $D_{w,i}$ in water phases, and it is essentially the reciprocal of the resistance a solute encounters on its route from the water to the storage site in the fish. The transport parameters $D_{w,i}$ can refer to diffusion, in which case $D_{w,i}$ equals $k.A.Z_w$, where k is the mass transfer coefficient (m/s), A is area of diffusion and Z_w is the chemical's fugacity capacity in the water phase. It can also refer to non-diffusive transport, where the solute is conveyed by a fluid flow G (m^3/s) such that $D_{w,i}$ equals $G.Z_w$. The overall transport parameter D_w can therefore also be expressed as $Q_w.Z_w$, where the transport parameter Q_w (m^3/s) combines all $k.A$ and flow rates G in water phases of the organism.

Similar to D_w all transport processes in lipid phases are combined in an overall lipid phase transport parameter D_l . This lipid phase parameter D_l can be designated $Q_l.Z_l$, where Z_l is the fugacity capacity of the lipid phase and Q_l combines all $k.A$ and flow rates G in lipid phases (e.g. membranes) of the organism. The reciprocal of D_l is the lipid-phase resistance. The transport parameters D_w and D_l therefore refer to the net transport of chemical in respectively the water and the lipid phase of the organism.

Assuming that the water and lipid transport processes apply in series it follows that the transport parameter for chemical exchange between the water and the organism D_f can be expressed as

$$1/D_f = 1/D_w + 1/D_l = 1/Q_w.Z_w + 1/Q_l.Z_l \quad (6)$$

Gobas and Mackay (1987) demonstrated that equation can be written in terms of rate constants k_1 and k_2 as

$$1/k_2 = V_L \cdot \{(K_{ow}/Q_w) + 1/Q_L\} \quad (7)$$

$$1/k_1 = V_L \cdot \{1/Q_w + (1/Q_L \cdot K_{ow})\} / L_f \quad (8)$$

The ratios V_L/Q_L and V_L/Q_w can be viewed as the times of chemical transport in V_L m³ of respectively lipids and water. However, if transport of a given amount of chemical requires a volume V of lipid, it will require a much larger volume i.e. $K_{ow} \cdot V_L$ of water, since the chemical concentration in the water is a factor of K_{ow} lower than in the lipids. The time for the water phase in the organism to transport a certain amount of chemical is therefore K_{ow} times longer than that for the lipid phase. The transport time of the water phase is therefore multiplied with K_{ow} in equation 7 and alternatively the lipid transport time is divided by K_{ow} in equation 8. Since the lipid and water transport processes occur in series these times are additive and the longer time "controls" the kinetics.

The expressions 7 and 8 contain two types of variables namely, (i) biological parameters i.e. V_L , Q_w , Q_L , G_v and L_f , which are specific to a particular fish and its physiological condition and (ii) a chemical parameter K_{ow} expressing the chemical's tendency to partition between lipids and water.

When for a series of chemicals, varying in K_{ow} , rate constants or uptake efficiencies have been determined in a particular organism equations 7 and 8 can be fitted to the experimental data to derive values for Q_w and Q_L . The data fitting involves a regression e.g. $1/k_1$ versus $1/K_{ow}$ or $1/k_2$ versus K_{ow} . Gobas and Mackay (1987) and Gobas et al. (1989) fitted equations 7 and 8 successfully to kinetic data in various fish species i.e. the rainbow trout, goldfish and guppy resulting in values for Q_w and Q_L . It was also found that Q_w increases with increasing body weight of the organism as

$$Q_w = 1.4 \cdot M^{0.6} \quad (9)$$

Although conclusive data are presently lacking there seems to be a similar relationship for Q_L i.e.

$$Q_L = 0.014 \cdot M^{0.6} \quad (10)$$

It thus transpires that the uptake and elimination rate constants of chemicals in fish are dependent on the fish's body weight and lipid content. Thus, as body weight and lipid content vary with time, uptake and elimination kinetics will also change. Some other factors have also been observed to affect k_1 and k_2 , namely the oxygen concentration in the water and water temperature.

Oxygen Concentration of Water : Norstrom et al. (1976) suggested a direct relationship between the ventilation volumetric rate (G_v) and the oxygen concentration in the water (C_oX) i.e.

$$G_v = A \cdot M^{0.8} / (E_{ox} \cdot C_{ox}) \quad (11)$$

where E_{ox} is the oxygen transfer efficiency across the gills, A is the metabolic rate coefficient ($\text{ml of } O_2 \cdot \text{h}^{-1} \cdot \text{g}^{-0.8}$) and M is the body weight of the organism. Equation 11 demonstrates that a drop in the oxygen concentration in the water leads to higher gill ventilation rate. This higher ventilation rate allows the fish to extract a larger amount of water to meet its oxygen requirements. Earlier we have seen that the gill ventilation rate is an important regulating factor in chemical uptake and elimination kinetics. It thus follows that C_{ox} will also affect the rate constants for chemical uptake and elimination. The extent to which C_{ox} affects k_1 and k_2 depends on the relative importance of the gill ventilation rate and other transport processes on k_1 and k_2 . For example, in a 750 g rainbow trout the water phase transport parameter Q_w consists of two processes i.e. the gill ventilation rate and other water transport processes, which can be designated as Q_1 . Both processes contribute equally to Q_w . In other words, half of the total water phase transport resistance i.e. $1/Q_w$ is due to the gill ventilation resistance i.e. $1/G_v$ and the other half is due to other water phase transport resistances i.e. $1/Q_1$. If the lipid phase transport resistance $1/Q_L$ can be ignored with respect to K_{ow}/Q_w (e.g. for a high K_{ow} chemical, such as hexachlorobenzene), $1/k_2$ is approximately $V_L \cdot K_{ow}/Q_w$ or $V_L \cdot K_{ow} \cdot (1/G_v + 1/Q_1)$. It thus follows that a drop in C_{ox} by a factor of 2 results in an increase in G_v by a factor of 2, and an increase in Q_w and k_2 of 33%. This demonstrates that a variation in the gill ventilation rate or oxygen concentration does not necessarily result in a similar variation in k_2 and k_1 . Only if Q_1 is small compared to G_v and Q_L can be ignored, an increase in gill ventilation rate is accompanied by a similar increase in k_2 and k_1 .

Temperature : Temperature can be shown to affect the uptake and elimination kinetics in two ways. First, it affects the fish's metabolic rate coefficient A (equation 11). For example, in the yellow perch (*Perca flavescens*) the active metabolic rate coefficient increases from 0.15 at 5°C to 0.37 $\text{mL } O_2 \cdot \text{h}^{-1} \cdot \text{g}^{-0.8}$ at 25°C (Neely 1979). Secondly, temperature usually affects the concentration of dissolved oxygen in the water. Norstrom suggested the following equation to express the oxygen concentration in the water C_{ox} (in mg/Kg) as a function of temperature T (in °C) under saturation conditions :

$$C_{ox} = 14.45 - 0.413 \cdot T + 0.00556 \cdot T^2 \quad (12)$$

As has been discussed above a reduction in C_{ox} can result in increase in the gill ventilation rate and uptake and elimination rate constants.

k_A & k_E : A lipid-water mass transfer model, similar to that discussed for k_1 and k_2 can also be developed for chemical

uptake from consumed food and elimination to faecal matter in the GI-tract. The derivation and validation of this model can be found in Gobas et al. 1988. It was shown that similar to equations 7 and 8 chemical specific relationships can be derived for the rate constants k_A and k_E and the chemical uptake efficiency from food E_{f0} i.e.

$$1/k_A = (V_F/G_I) \cdot \{(G_O \cdot L_G/Q_{WF}) \cdot K_{OW} + (G_O \cdot L_G/Q_{LF}) + 1\} \quad (13)$$

$$1/k_E = (V_F \cdot L_F/G_O \cdot L_G) \cdot \{(G_O \cdot L_G/Q_{WF}) \cdot K_{OW} + (G_O \cdot L_G/Q_{LF}) + 1\} \quad (14)$$

$$1/E_{f0} = (G_O \cdot L_G/Q_{WF}) \cdot K_{OW} + G_O \cdot L_G/Q_{LF} + 1 \quad (15)$$

where G_I is the volumetric feeding rate (in m^3 food per hour), G_O is the volumetric egestion rate (in m^3/h), Q_{WF} is the water phase transport parameter for chemical exchange between the GI-tract and the final storage site in the organism (in m^3/h), Q_{LF} is the lipid phase transport parameter for chemical exchange between the GI-tract and the final storage site in the organism (in m^3/h) and L_G is the organic or "lipid" fraction of the gastro-intestinal contents (in grams of organic matter per gram of GI contents).

The reciprocal of k_A , i.e., $1/k_A$, can be viewed as the time needed to transport chemical from the food into the fish or as the total resistance for chemical transfer from the food into the fish. Likewise, $1/k_E$ is the time required to eliminate chemical from the fish into the faeces or the total resistance for chemical elimination to the faeces. The ratios $(V_F/G_I) \cdot (G_O \cdot L_G/Q_{WF}) \cdot K_{OW}$ and $(V_F/G_I) \cdot (G_O \cdot L_G/Q_{LF})$ can be viewed as the solute's relative transport times in the water and lipid phases, respectively, of the fish or as the relative resistances that the solute encounters in the water and lipid phases of the fish on its route from the food phase in the GI-tract to the final storage site in the body lipid of the fish. When the solute's K_{OW} increases, and aqueous solubility thus decreases, the water phase of the fish can accommodate only a lower concentration of solute molecules. As a result, the time required to transport a certain amount of solute with this lower concentration increases. The resistance of the fish's water phase toward mass transfer thus increases, whereas it remains approximately constant in the lipid phase. For high K_{OW} chemicals, this implies that the uptake rate from food and elimination rate to the faeces and thus k_A , E_{f0} and k_E decrease with increasing K_{OW} . For low K_{OW} chemicals, uptake from food and elimination by excretion to the faeces is predominantly controlled by transport in lipid phases, and k_A , E_{f0} , and k_E are approximately constant with respect to K_{OW} .

Equation 15 demonstrates that experimental measurements of E_{f0} for a series of chemicals with varying K_{OW} under controlled conditions, i.e., a constant feeding rate and no uptake of chemical from the water, enable the fundamental kinetic parameters Q_W and Q_L to be determined. Knowledge of these

parameters is invaluable for reliable estimation of organic chemical bioaccumulation from contaminated food.

Gobas et al. (1988) showed that experimental data for dietary uptake of chemicals in fish fit this simple relationship with values for $(G_o \cdot L_g / Q_u)$ of $5.3 (\pm 1.5) \cdot 10^{-8}$ and for $(G_o \cdot L_g / Q_L + 1)$ of $2.3 (\pm 0.3)$, thus resulting in the following relationship for E_{f0} , k_A and k_E

$$1/E_{f0} = 5.3 \cdot 10^{-8} \cdot K_{ow} + 2.3 \quad (16)$$

$$1/k_A = (V_f / G_i) \cdot (5.3 \cdot 10^{-8} \cdot K_{ow} + 2.3) \quad (17)$$

$$1/k_E = (V_f \cdot L_f / G_o \cdot L_g) \cdot (5.3 \cdot 10^{-8} \cdot K_{ow} + 2.3) \quad (18)$$

The relationships that have been presented above for the chemical uptake and elimination kinetics have been experimentally validated in several species of fish (Gobas and Mackay 1987, Gobas et al. 1988 & 1989). For other aquatic organisms relationships for the uptake and elimination rate constants similar to those discussed above have yet not been established, largely as a result of a lack of experimental data. However, it is believed that when these experimental data become available similar relationships can be derived for aquatic organisms other than fish.

Chemical Dynamics in Benthic Invertebrates

Reuber et al. (1987) and Pavlou and Weston (1984) have suggested that organic chemical concentrations in benthic invertebrates and sediments may be at chemical-equilibrium. The relationship between organism and sediment concentrations can then be expressed as

$$C_B / C_u = L_B \cdot K_{ow} / X_s \quad (19)$$

where L_B is the lipid fraction of the organism, X_s is the organic fraction of the sediment and K_{ow} is the 1-octanol-water partition coefficient of the chemical. Field experiments in Lake St. Clair with mayflies (*Hexagenia limbata*) indicate that benthic invertebrates and sediments are indeed at or near chemical equilibrium (Gobas et al. 1989). Although more experimental are needed to properly validate equation 19, the chemical equilibrium model gives a satisfactory initial description of the chemical distribution between sediments and benthic invertebrates. Since the sediments are a large compartments with a high storage capacity for organic chemicals variations in chemical concentrations in the sediments due to spill events can usually be considered small. Since studies by Landrum and Poore (1988) suggest that the chemical uptake and depuration kinetics in benthic invertebrates is relatively fast it can often be assumed that chemical concentrations in sediments and benthic

invertebrates are at steady-state. Unless changes in chemical concentrations in the sediments change very rapidly equation 19 is believed to give an satisfactory description of chemical dynamics in benthic invertebrates. More experimental data are needed to improve the model predictions.

Trophic Interactions

It has been demonstrated that concentrations of various organic chemical, especially those which have high 1-octanol-water partition coefficients (i.e., $\log K_{ow}$ above 6), tend to reach higher levels in organisms of higher trophic status. This indicates that chemical transfer through the food-chain can significantly contribute to the body burden of biota. Models of food-chain transfer thus require information regarding the trophic interactions in the affected ecosystem. If available, this information can be introduced in the ECOTOX model. However, in general, it appears to be difficult to determine food-webs and trophic interactions. As a result information of the trophodynamics (i.e. predator-prey relationships) is often not available. In that case ECOTOX simulates a pelagic and a benthic food-chain, consisting of 5 trophic compartments. For example, in the pelagic food-chain small fish (e.g. 1 g) feed on algae, larger fish (e.g. 10g) feed on the small fish, large fish (e.g. 100g) feed on the smaller 10 g fish and very large fish (e.g. 1000 g) feed on the 100g fish. The benthic food-chain is similar but benthic organisms are the basis of food-chain. It should be noted this rather simplistic picture of the food-chain is only used when no information of the actual food-chain interactions are available. However, it is encouraging that simple linear food-chain transfer models, such as the one used by ECOTOX, has been shown to fit real field data remarkably well (Thomann 1988).

Toxicity

Toxic effects due to chemical exposure can be expected when the body burden of the chemical in the organism reaches a certain threshold level. For a large class of chemicals such as chlorinated alkanes and aromatics, alcohols, ketones and others, it has been shown that acute lethality is achieved when the body burden of the chemical reaches a concentration of approximately 1 to 10 mmol/kg (McCarthy 1987). Abernethy and Mackay (1987) demonstrated that this acute toxic threshold level is relatively universal between aquatic organisms and independent of the chemical properties of toxicant as long as the toxicants act by the same toxic ("narcotic") mode. In other words, the same body burden of approximately 1 to 10 mmol/kg causes the same acute toxic effect in most aquatic organism. The threshold level for chronic lethal toxicity is approximately 10 times below the acute toxic threshold level i.e. 0.1 to 1 mmol/kg. Since ECOTOX

predicts the concentration of chemicals in the organism as a function of time, it can simply compare the predicted body burden in the aquatic organisms with the toxic threshold levels to indicate when and where in the food-chain acute or chronic toxic conditions exist.

Toxicity of mixtures

The mechanism of toxic action, described above for some chemicals with a "narcotic" mode of action, appears to be associated with a certain mole or volume fraction of chemical at the toxic site. The nature of the chemical species is relatively unimportant. It has therefore been suggested that as long as chemicals act by the same "narcotic" mode of action each absorbed substance contributes to the toxic effect. The toxic effect can thus be treated as the sum of the toxic contributions of the individual chemical components i.e. the toxicity is additive. Since the toxic contribution of a chemical is a direct function of its concentration in the organism the combined toxic effect of a series of chemical substances can be derived as

$$\sum X_i/V_f$$

where X_i is the amount of chemical i in mmoles and V_f is the volume of the organism (in kg) and i are the number of chemical substances in the mixture. When $\sum X_i/V_f$ reaches 1 to 10 mmol/kg acute lethality is predicted.

EXAMPLES

Two examples will be presented to illustrate the use of ECOTOX. The first example illustrates the effects of a single spill of carbontetrachloride. The second example simulates the food-chain response to a periodically reoccurring spill of hexachlorobenzene.

Example I

Model Parameterization

Input :

- (1) The water concentration C_w during the spill event : C_w increased from 0.001 ng/L to 32 ug/L, then returned to the background level
- (2) The sediment concentration C_s during the spill event : C_s increased from 1.8 ng/kg to 300 ug/L, then returned to the background level
- (3) 1-Octanol-water partition coefficient : $10^{2.64}$
- (4) Metabolic transformation rate constant k_R : 0.1 d^{-1}

- (5) Organic carbon fraction of the sediment X_s : 0.025
- (6) Lipid fraction of benthic invertebrates : 0.06 (default)
- (7) Lipid fraction algae & zooplankton : 0.005 (default)
- (8) Dissolved organic carbon fraction of the water : 10^{-6} kg/L (default)
- (9) Initial weight fish 1 : 1 g (default)
- (10) Initial weight fish 2 : 10 g (default)
- (11) Initial weight fish 3 : 100 g (default)
- (12) Initial weight fish 4 : 1000 g (default)
- (13) Initial lipid fraction fish 1 : 0.03 (default)
- (14) Initial lipid fraction fish 2 : 0.06 (default)
- (15) Initial lipid fraction fish 3 : 0.09 (default)
- (16) Initial lipid fraction fish 4 : 0.012 (default)
- (17) Growth rate constant : 0.002 d^{-1} (default)
- (18) Lipid fraction variation : 0.00041 d^{-1}
- (19) Feeding rate G_i of fish 1,2,3,4 : 2% of the fish's body weight per day (default)
- (20) Water temperature : 20°C
- (21) Trophic Interactions : algae→fish1→fish2→fish3→fish4 (default)

The model output is illustrated in Figure 1. It predicts the highest concentration of carbontetrachloride (i.e. approximately 316 ug/kg) in small, 1g fish. The larger fish reach somewhat lower concentrations of 79, 32 and 13 ug/kg for fish 2,3 and 4 respectively. In algae and benthic invertebrates the maximum concentration is approximately 35 ug/kg. The predicted body burdens in aquatic organisms are well below the acute lethal dose of 1 to 10 mmol/kg or 154,000 ug/kg. The spill is therefore expected not to cause immediate lethality. Clearance of carbontetrachloride in algae and benthic invertebrates is fast resulting in virtual complete elimination when carbontetrachloride concentrations in the water have returned to their background levels. Among the fish species, small, 1g fish have the highest clearance rates. After approximately 60 days after the spill the body burdens of the small 1g fish have returned to their original background level. Figure 1 illustrates that the time required for complete clearance of carbontetrachloride is longer in the larger fish and tends to increase with increasing body weight. The largest fish thus have the slowest depuration rates and their clearance time is the longest.

Example 2

Model Parameterization

Input :

- (1) The water concentration C_w during the spill event : C_w increased from its background level of 1 ng/L to 100 ng/L in january, march, july and september due to spill events and

returned to background levels in 8 days after each spill event.
 (2) The sediment concentration C_s during the spill event : C_s remained approximately constant at 10,000 ng/kg throughout the year.

- (3) 1-Octanol-water partition coefficient : $10^{5.45}$
- (4) Metabolic transformation rate constant k_R : 0 d^{-1} (default)
- (5) Organic carbon fraction of the sediment X_s : 0.025
- (6) Lipid fraction of benthic invertebrates : 0.06 (default)
- (7) Lipid fraction algae & zooplankton : 0.005 (default)
- (8) Dissolved organic carbon fraction of the water : 10^{-6} kg/L (default)
- (9) Initial weight fish 1 : 1 g (default)
- (10) Initial weight fish 2 : 10 g (default)
- (11) Initial weight fish 3 : 100 g (default)
- (12) Initial weight fish 4 : 1000 g (default)
- (13) Initial lipid fraction fish 1 : 0.03 (default)
- (14) Initial lipid fraction fish 2 : 0.06 (default)
- (15) Initial lipid fraction fish 3 : 0.09 (default)
- (16) Initial lipid fraction fish 4 : 0.012 (default)
- (17) Growth rate constant :

Small 1g fish : 0.002 d^{-1} throughout the year

10g fish : No increase in body weight until mid-february
 Growth from 10g in mid-february to 15.5 in mid-november

No growth after mid-november

100g fish : No increase in body weight until mid-february
 Growth from 100g in mid-february to 110g in mid-november

No growth after mid-november

1000g fish: No increase in body weight until mid-february
 Growth from 1000g in mid-february to 1200 in mid-november

No growth after mid-november

(18) Lipid fraction variation

1g fish : constant lipid fraction of 0.03 throughout the year

10g fish: A constant drop in lipid fraction from january to mid-february from 0.06 to 0.032.

A constant increase in lipid fraction with time from 0.032 in mid-february to 0.09 in mid-november.

A constant drop in lipid fraction from 0.09 in mid-november to 0.08 at the end of december.

100g fish: A constant drop in lipid fraction from january to mid-february from 0.09 to 0.06.

A constant increase in lipid fraction with time from 0.06 in mid-february to 0.15 in mid-november.

A constant drop in lipid fraction from 0.15 in mid-november to 0.12 at the end of december.

1000g fish: A constant drop in lipid fraction from january to mid-february from 0.12 to 0.09.

A constant increase in lipid fraction with time from 0.032 in mid-february to 0.20 in mid-november.

A constant drop in lipid fraction from 0.20 in mid-

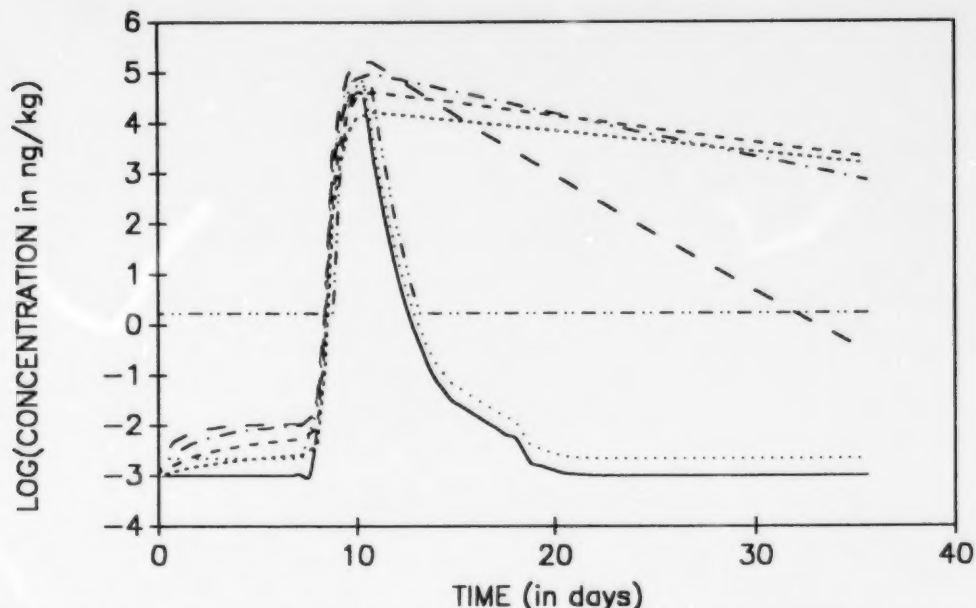


Figure 1 : Ecosystem response as a result of single spill of carbontetrachloride (water: solid line _____; algae: dotted line; small, 1g fish: long dashed line _____; small, 10g fish: dash-dot line - . - . - .; large 100g fish: medium dashed lined - - - -; very large, 1000g fish: short dashed line -----).

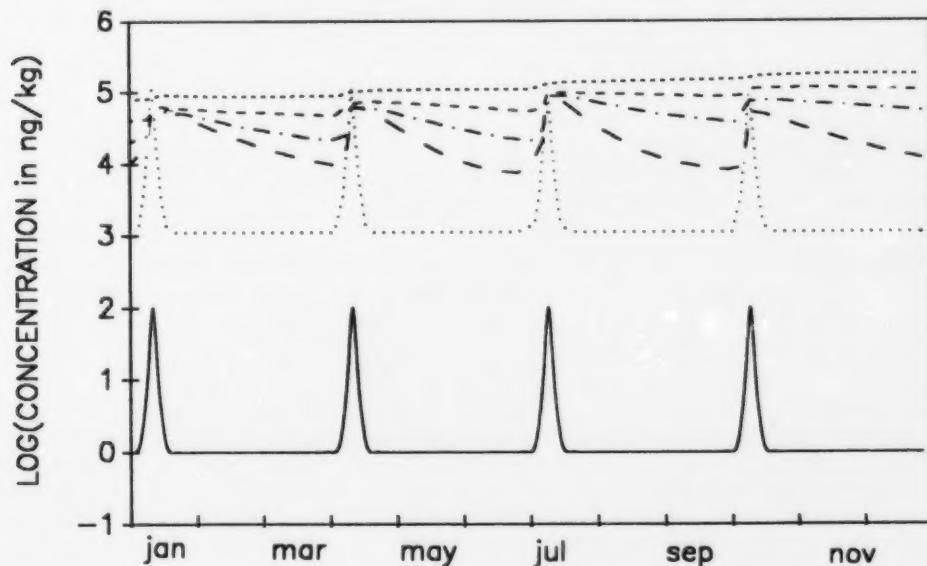


Figure 2 : Ecosystem response as a result of a reoccurring spill of hexachlorobenzene (water: solid line _____; algae: dotted line; small, 1g fish: long dashed line _____; small, 10g fish: dash-dot line - . - . - .; large 100g fish: medium dashed lined - - - -; very large, 1000g fish: short dashed line -----; benthic invertebrate: dash-dot-dotted line - . . - . . - . .).

- november to 0.16 at the end of december.
- (19) Feeding rate G_i of fish
 fish 1: 2% of the fish's body weight per day (default)
 fish 2,3,4: no feeding until mid-february
 2% of the fish's body weight per day from mid-february to mid-november
 no feeding after mid-november
- (20) Water temperature : constant at 4°C mid-february, then increasing to 15°C until june. From june to august the temperature remains constant. Then it drops back to 4°C, to remain constant at 4°C until mid-november.
- (21) Trophic Interactions :

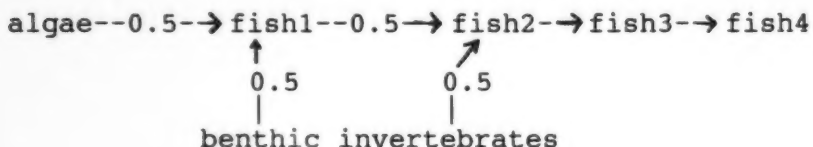


Figure 2 illustrates the model output. It shows that after every spill event hexachlorobenzene concentrations in algae and fish peak and then, as the concentration in the water has returned to its background level, tend to drop to their original levels. Hexachlorobenzene concentrations in algae return to their original levels very quickly. The clearance rates in fish, however, are much slower. During the two month periods between the spills hexachlorobenzene concentrations in small, 1g fish are able to return to their original levels, thus indicating that complete clearance occurs in approximately two months. For the larger fish the two month periods between two successive spill events are too short for complete clearance. After each spill event the concentration in the fish reaches a level which is higher than that after the previous spill. This effect is most profound in the largest fish, which have the slowest clearance rates. As a result, hexachlorobenzene concentrations in the larger fish tend to reflect the maximum concentration in the water during the spill rather than the mean or background levels during the year. The highest concentration of hexachlorobenzene (i.e. approximately 126 ug/kg) is reached in the 1000g fish after the fourth spill. However, continuation of this scenario would have resulted in even higher concentrations of hexachlorobenzene in the fish. The predicted body burdens in the aquatic organisms are below the acute lethal dose of 1 to 10 mmol/kg or 285,000 ug/kg. This spill scenario is therefore expected not to cause immediate lethality.

ACKNOWLEDGEMENTS

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THE JUXTAPOSITION OF LONG-TERM AND REAL-TIME OIL SPILL MODELLING

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ABSTRACT

Generalized long-term and real-time oil spill models are compared. The influence of grid element size in the long-term model domain, the size of the time step in each of the models, and the ways in which the data are presented are assessed. Additionally, the sensitivity analysis of a long-term model, which typically includes only the over and under estimation of environmental forces, is extended to examine factors that are found to vary in real-time spill scenarios. This includes parameters such as the oil composition and flow rate, and the spatial and temporal resolution of the natural forces which affect the oil behaviour. The extent to which the feedback mechanism of behaviour verification, available in real-time modelling, affects the perceived usefulness of the hindcast information is described.

The condensate blowout from the Uniacke G-72 wellsite in 1984, off Canada's east coast, is presented as a case study. The results from the long-term oil spill model used in the Contingency planning for the wellsite are compared to the results generated by the real-time modelling of the spill. The matrix of results is expanded by rerunning the long-term model using the conditions known to exist during the spill incident. The extent to which the long-term model is sensitive to these real-time conditions is shown to be instructive as an aid to the interpretation of the long-term modelling information contained in the contingency plan.

INTRODUCTION

One of the early considerations in an oil spill response strategy is an assessment of the severity of the situation. Within the spill contingency plan documentation the results of an oil spill trajectory analysis are designed to aid the response team in evaluating such issues as:

- shoreline impacts;
- impact on biologically sensitive areas;
- sites for control centres for clean up crews; and,
- the logistical requirements to implement spill countermeasures.

The spill trajectory information typically available in the contingency plan includes maps of areal extent of the slick associated with various probabilities of occurrence of oil. In addition, the average and maximum expected slick speed is provided, as well as some sort of risk analysis of shoreline contact. These results are often presented on a monthly basis. A seasonal 'worst case' scenario may also be described, based on a combination of environmental circumstances that present the greatest potential hazard.

Very quickly, however, the response team requires further oil spill behaviour information. The focus soon shifts to the slick of the particular incident, and answers regarding its predicted position, areal coverage, thickness and potential threat to specific locations are needed.

This paper addresses the generalized computer methodology used in oil spill behaviour modelling. The emphasis is placed on the basic differences between the long-term models, used to prepare contingency plans, and the real-time models applied to predicting the behaviour during an oil spill incident. The intent of the paper is to identify key features in each of the two models that will allow the end-users to rationalize the differences that are sometimes apparent in the models' results.

OVERVIEW

In order to compare the two modelling approaches, a description of each model is required. Following this, the data typically used to run the models, and the information provided by each model, are reviewed. Finally a comparison is made of the modelling results based on an actual spill; the Uniacke G-72 blowout on the Scotian Shelf in February 1984. This case demonstrates that although the results of the models differed, they could both be used to assess the threat to Sable Island, 20 km to the south.

LONG-TERM SPILL MODELS

Reviews of the many existing long-term oil spill models (Davidson and Lawrence, 1982; Spaulding, 1988) underscore the various means by which it is possible to produce computer-derived slick behaviour information for contingency plan use. The differences, however, relate primarily to the nature of the environmental input data, and the algorithms used to represent advection and weathering of the oil. The structures of the models, within which these various mechanisms operate, are very similar.

Essentially the model study area, that is the geographical region which encompasses the area likely to be affected by a spill, is digitized into a spatial grid array. The area represented by each grid element (which is coded as being land, water, ice, etc.) is defined by the modeller and dictates the spatial resolution of a model. Figure 1, as an example, shows the domain of two models, one digitized at $1/4^\circ$ latitude by $1/4^\circ$ longitude and the other at $1/10^\circ$ by $1/10^\circ$.

The environmental forces driving the trajectory, such as wind and current, may be spatially variable at the same resolution of the model (i.e. on a grid element by element basis), or may be applied over several grid elements, or even the entire model domain.

The position of the centroid of a surface slick is evaluated by a 'transport' algorithm. This simulates the advection of the surface flow, which carries the oil, by vectorially summing the relevant environmental factors. The time step of the model reflects how often the slick position is updated. Typical contingency plan models adopt a time step of 1 day, over a simulation period of say 20 years. The time step is defined by the modeller to complement the environmental data available.

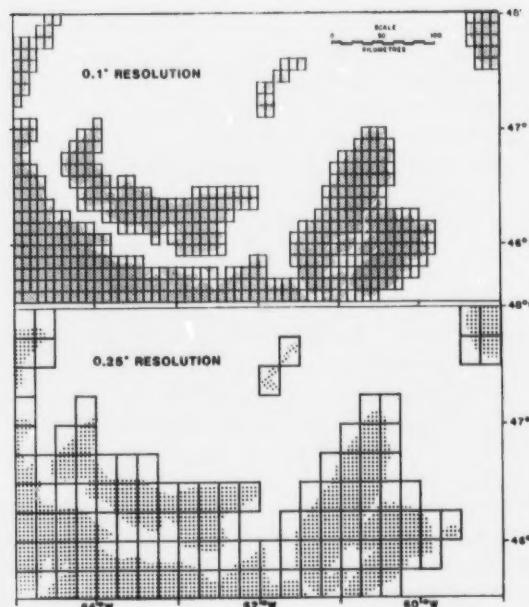


FIGURE 1. THE GULF OF ST. LAWRENCE LONG-TERM OIL SPILL MODEL DOMAIN AT TWO SPATIAL RESOLUTIONS. A) GRID ELEMENT SIZE $1/10^\circ$ LATITUDE BY $1/10^\circ$ LONGITUDE. B) GRID ELEMENT SIZE $1/4^\circ$ LATITUDE BY $1/4^\circ$ LONGITUDE.

At each time step the characteristics of the slick are updated by using a 'transport' algorithm to determine the slick's new position, and a 'weathering' algorithm to simulate the change in the slick due to evaporation, emulsification, dispersion, etc. This computed information (i.e. position, volume remaining on the surface, percent oil evaporated, etc.) is labelled by the model for subsequent processing in terms of a grid element (spatial) and number of time steps elapsed since the start of the simulation (temporal). After the model has completed the generation and archival of this data, a post-processor is used to produce the information included in the contingency plan.

REAL-TIME SPILL MODELS

The purpose of real-time spill modelling is to make useful forecasts of slick behaviour available to the oil response team during an actual spill event. Because results are often needed quickly, speed of execution is a requirement of these models. This speed is achievable in large part because of the smaller volume of input and output data processed rather than a faster method of simulating the spill. In fact, the 'transport' and 'weathering' algorithms used in real-time models are not very different from those used in the long-term models.

The real-time model uses site specific environmental data to predict, on the order of hours or days, the fate of a particular type of oil released at

a known location. The spatial and temporal scales are therefore much smaller than those found in long-term models. This change in scale introduces factors in real-time modelling that are not significant in long-term modelling. For instance, by reducing the time step from one day to one hour advective processes, such as tidal currents, and weathering processes, such as the evaporation of the volatile components of the oil spilled, need to be considered.

USING THE MODELS

In order to achieve an acceptable statistical validity to the information presented in the contingency plan the long-term model simulates many hundreds of spills. Relevant data from each of these simulated spills are combined and analysed to determine an ensemble statistic. On the other hand real-time modelling, which is interested in only one single event, involves little statistical averaging.

Within contingency plans the model produced 'probability maps' are often used by the oil spill response team when it initially assesses the severity of a spill. These maps are intended to reveal a contour around the spill location representing the area within which one could expect oil from the spill to be found with an associated probability. The model produces these maps by assigning a probability of occurrence to each grid element based on the number of times oil entered that grid during the run and then drawing an envelope encompassing all the elements having the required probability based on the total number of slicks. As such they represent where a certain percentage of the slicks may be expected to be found. It is worthwhile to note that, as shown in Figure 2, the spatial resolution of the model can significantly alter the perceived severity of a spill.

Slick trajectories are developed by taking a sequence of driving forces and consecutively applying them to the slick position, starting with the release point of the oil. Figure 3 illustrates this process. Threats to selected areas within the model domain, such as shoreline, are determined by the number of trajectories that encounter, or approach, the region of interest. Trajectories can be generated by real-time models but oil slick position plots may also be provided. Figure 3 also shows the spill position plot. It can be seen that under certain circumstances the difference between these presentations can be significant in assessing risk to selected areas.

Sensitivity analysis, where the best estimate of the input data used in the initial run is forced to vary to allow for the uncertainties expected in the data-set, are undertaken with both long-term and real-time modelling. The former models usually vary the wind speed and direction, or current speed and direction, and reflect our limited understanding of marine climatology. The model is then rerun, usually by varying only one parameter at a time, and the results included in the contingency plan.

Real-time modelling incorporates a manner of sensitivity analysis based on a feedback mechanism. This is due to the real-time monitoring of the slick that goes on during a spill event. If, for example, the slick is reported to be travelling consistently faster than the model predicts, then the model can be adjusted and rerun in order to match the observations. Using this feedback mechanism the real-time model is being tuned to better

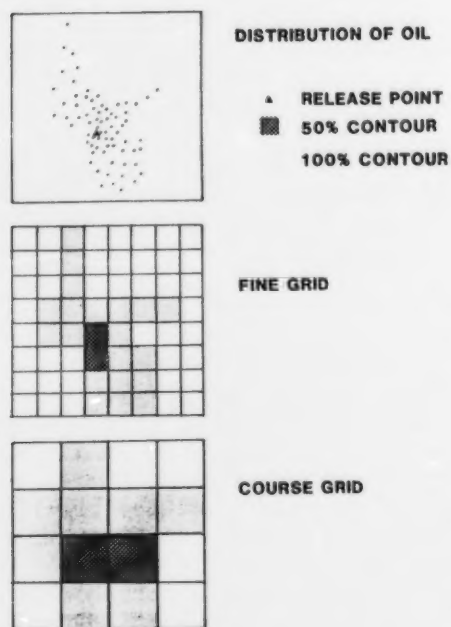


FIGURE 2. A COMPARISON OF THE CONTOURS OF THE PROBABILITY OF OCCURRENCE OF OIL AS A FUNCTION OF GRID ELEMENT SIZE.

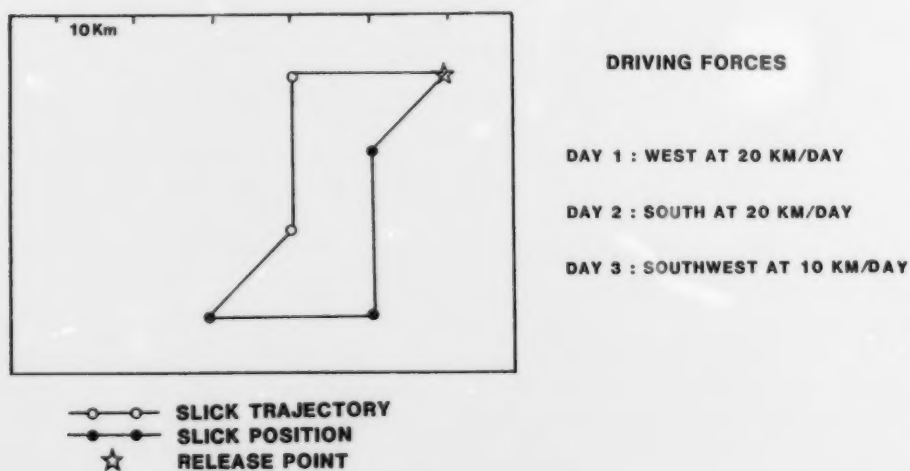


FIGURE 3. A COMPARISON OF THE PRESENTATION METHODS FOR THE LOCATION OF A SLICK USING A THREE DAY EVENT.

represent the actual situation each time it is run. This facility is particularly useful during events that vary appreciably from 'normal' conditions.

The real-time models can also vary parameters, such as flow rate or oil composition, with time. Within a few runs, the real-time model may be simulating an oil spill using parameters quite distinct from those expected, and used to govern, the long-term model. This also allows the model to be used in the 'what if' mode where various circumstances that may arise can be examined.

THE UNIACKE G-72 SPILL

Shell Canada Resources Limited et al., while testing the Uniacke G-72 well using the semi-submersible drilling unit SDS Vinland, experienced an uncontrolled release of gas at 2230 h Atlantic Standard Time (AST) on February 22, 1984. The flow of gas and condensate through the rotary table on the drilling floor of the Vinland continued for 10 days until the well was brought under control on March 3, 1984. The initial flows from the well were estimated to be between 1.11 and 1.83×10^6 m³/day (40-60 million ft³/day) of gas and upwards of 48 m³/day (300 barrels) of condensate (Martec, 1984). The flow rate was observed to diminish throughout the course of the blowout.

The Uniacke wellsite is located on the Scotian Shelf at 44°11'29.07"N, 59°41'09.4"W, 20 km north of the eastern tip of Sable Island in 158 m of water (Figure 4).

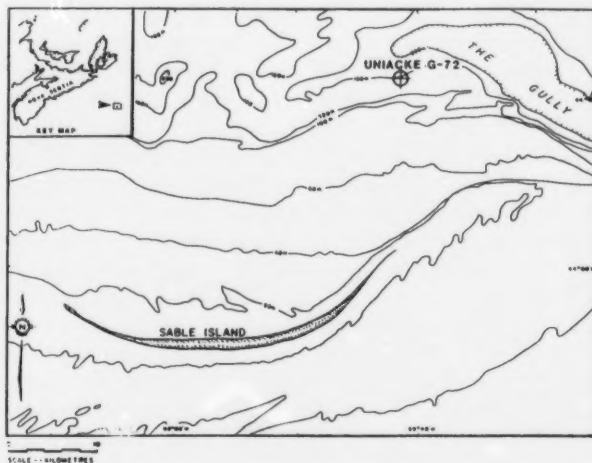


FIGURE 4. THE LOCATION OF THE UNIACKE G-72 WELLSITE.

Immediately after the blowout commenced, Shell's Spill Contingency Plan was implemented. This plan included provisions for containment, clean-up, and an environmental monitoring program. Computer modelled slick information was available from both long-term models (in the Contingency Plan documentation) and by real-time spill modelling.

Table 1 lists input data to the long-term model as well as output that was of immediate relevance to the spill response team. Due to the end of month start time of the spill, both the results of the February and March analyses were considered relevant.

TABLE 1. SUMMARY OF RELEVANT LONG-TERM MODEL DATA FOR UNIACKE SPILL

Time Step:	1 day
Grid Size:	1/4° latitude by 1/4° longitude
Oil Type:	Scotian Shelf Crude - API gravity 35°
Spill Size:	1000 barrels/day
Wind Data:	20 years of speed and direction recorded on Sable Island on 5° x 5° grid
Current Data:	Synthesis of known residual flow on 1/2° x 1/2° grid
Sensitivity Analysis:	Wind speed ±10%, wind direction ±10° Current speed ±50%, current direction ±45°
Average Slick Speed:	20 km/day
Maximum Slick Speed:	60 km/day
Probability of Mainland Contact:	Negligible
Probability of Sable Island Contact*:	30%
Travel Time to Sable Island*:	1-11 days
Percentage of Oil on Surface at Contact with Sable Island*:	3-18%
*based on slick trajectories	

The initial conditions for the real-time model, given in Table 2, are significantly different from the long-term model parameters. As monitoring information of the slick's fate was received by the response team further adjustments were made which included:

- a) flow rate reduction
- b) wind vector rotated 20°, then 40°, clockwise
- c) slick thickness of 40 nanometres to represent loss of slick visibility
- d) slick considered incoherent and not modelled after 5 days elapsed since release.

TABLE 2. SUMMARY OF INITIAL REAL-TIME MODEL DATA FOR UNIACKE SPILL

Time Step:	1 hour
Spill Size:	300 barrels/day
Wind Data:	Synthesis of reports from weather station on Sable Island, monitoring vessels and three drilling rigs operating on Shelf. Forecasted wind data from both public and private agencies.
Current Data:	Tidal current: M_2 barotropic tide on $4' \times 4'$ grid; residual flow on $1/2' \times 1/2'$ grid as in long-term model.
Predicted Contact With Sable Island: (based on slick position)	
Day 6 of Spill:	Within 12 hours of release - up to 50% of oil remaining
Day 7 of Spill:	36 to 48 hours after release - 8 to 12% of oil remaining
Day 8 of Spill:	60 to 72 hours after release - 4 to 8% of oil remaining
Day 9 of Spill:	60 to 72 hours after release - 6 to 10% of oil remaining

In comparing the two model results it can be seen that the threat to Sable Island, presented in the contingency plan for a long-term model, is reasonably consistent with the real-time model prediction. In fact, there was no physical evidence of the condensate contacting Sable Island as a coherent slick and, if the spill had not been brought under control as quickly as it was, the real-time model would have been tuned further to reflect this. This does not represent a contradiction to the long-term model results as its calculated probability of contact with the Island was 30 percent.

The long-term model was rerun using conditions observed during the spill event. The results support the contention that the condensate experienced a high evaporative flux as it was jetted onto the sea surface. Having settled as a surface slick evaporation proceeded at a slower rate as many of the volatile components had already flashed. The probability of Sable Island contact was actually increased, but with a reduced volume of condensate to below significantly detectable levels.

CONCLUSION

As a consequence of the points described above, the oil spill response team should expect the results produced by long-term and real-time models to

differ. The implication being that with an ability to rationalize these differences both sources of information can be used to full advantage. This can be accomplished via spill exercises and/or seminars that involve the modellers and other members of the response team. Not only does this foster an ongoing assessment of the modelling process, but gives the spill response team a confidence in the models' results which allows them to do their job more effectively.

ACKNOWLEDGEMENTS

Recognition is due the Canada Oil and Gas Lands Administration, and to Shell Canada Resources Limited, for their efforts in furthering the advance of oil spill modelling technology.

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OIL POLLUTION PROBLEM IN THE BALTIC MARINE ENVIRONMENT

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ABSTRACT

The Baltic Sea, a large brackish water basin, is situated in Northern Europe and surrounded by seven countries. The Baltic Sea, therefore provides an important means of transportation in the northern part of Europe and to the Atlantic ocean. The narrow routes of the Baltic Sea with heavy marine traffic constitute a severe risk of various environmental accidents. The proposed offshore oil-activities in the southern part of the Baltic Sea will also increase the risk of pollution. Attempts to combat and collect oil during the winter under prevailing subarctic conditions have proved to be inefficient in the case of large oil spills.

In this article we will review factors determining the severity of oil spills in the Baltic Sea. Furthermore, we will provide recent statistics on the sources and effects of petroleum hydrocarbons. Some of the earlier and recent spill experiences have been chosen to describe the spill problem in the Baltic sea.

INTRODUCTION

The Baltic is one of the most investigated sea areas in the world. It has spawned extensive literature dealing with oceanographical, biological and ecological studies. The first scientific documents were published during the beginning of this century.

Based on the scientific knowledge of the Baltic marine environment it can be concluded that some of the environmental changes observed during this century can be attributed to natural causes alone, while others are partially or solely caused by human activities (Melvasalo 1981).

The Baltic sea joins together seven nations of different political and economical structure, totalling over 70 million people. Due to man's intensive utilization of the Baltic and its catchment area, the natural systems are stressed not only by the naturally low salinity but also by severe pollution

from land, air and transport by sea. The greatest concern has been directed towards the levels and effects of chlorinated hydrocarbons, heavy metals, nutrients and oil.

The following review concerns the oil pollution problem in the Baltic Sea. It will briefly describe the environmental features of the Baltic, which is needed to understand the factors determining the severity of oil (spills) in this isolated and sensitive brackish water environment.

BASIC FEATURES OF THE BALTIC SEA

Morphometry

The Baltic is one of the largest brackish water areas in the world. It extends over an area of 415,000 km² including the shallow estuary of about 42,000 km² (Falkenmark and Mikulski 1974). The Baltic can be described as an enormous "fjord" with a shallow and narrow entrance to the North Sea (TABLE 1 and FIGURE 1). It is a complicated system of gulfs, bays and coastal archipelagos, which create a long coastline. The straight length of the Baltic coastline measures 11,000 km (HELCOM 1987). If all configurations of the coasts are taken into account, the coastline becomes much longer, e.g. the coastline of Finland reaches a length of about 39,000 km (Atlas of Finland 1986).

TABLE 1. The basic features of the Baltic Sea.

Catchment area	1,669,459	km ²
Population density	70,748,000	persons
Sea area		
excluding estuary	372,730	km ²
including estuary	415,125	"
Basin volume	21,714	km ³
Length of coastline (straight length)	10,720	km
Mean depth	38 - 68	m
Maximum depth	459	m
Water temperature (summer stratification)		
surface, 0-20 m	15 - 18	°C
subsurface, 20-70 m	0 - 3	°C
bottom > 70 m	3 - 5	°C
Salinity	0.5 - 1.0	‰
Water renewal time	25 - 40	years

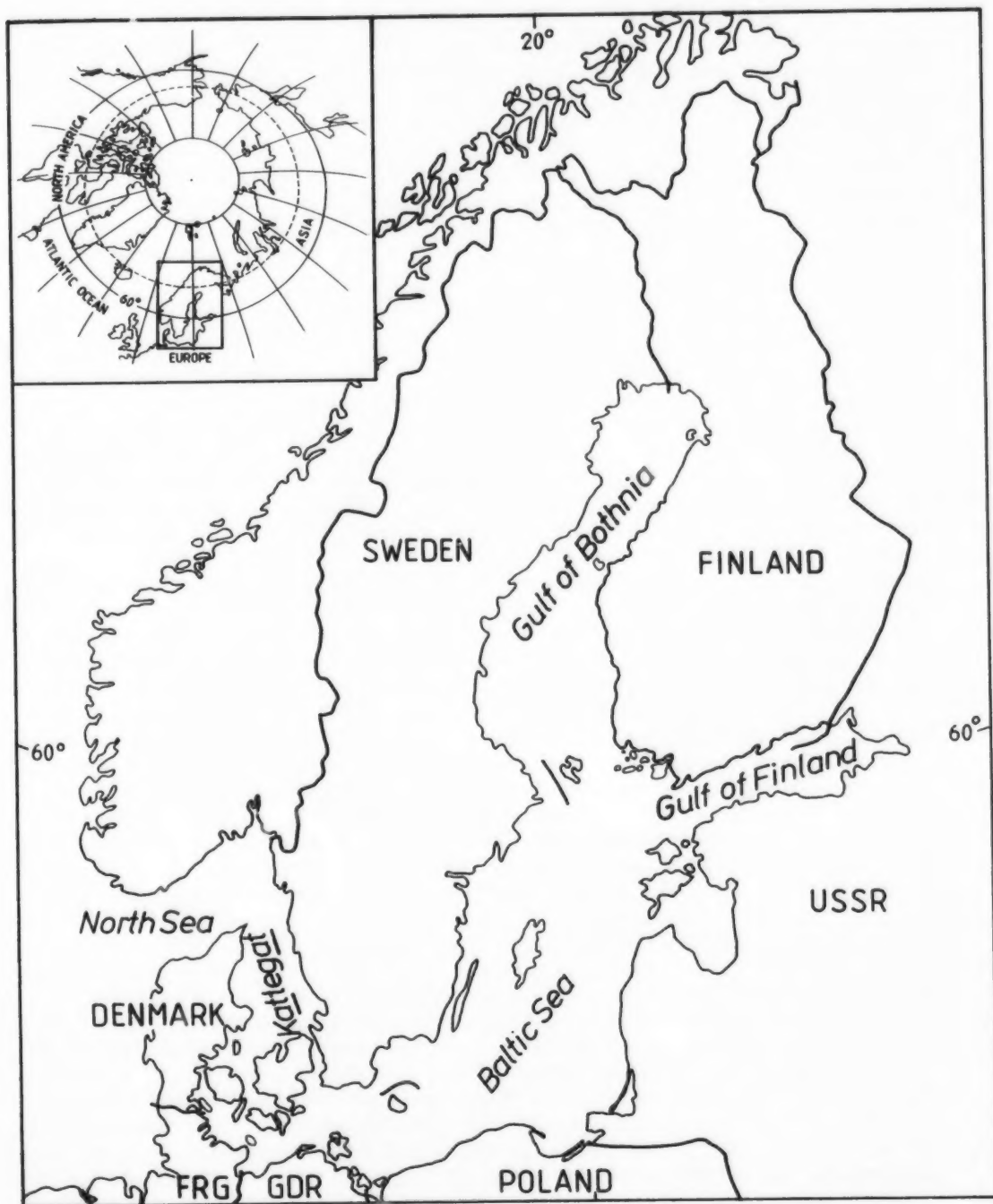


FIGURE 1. Index map of the Baltic Sea area.

The volume of the basin has been measured to be 22,000 km³. This is not very much compared to its area, which is caused by the shallowness of the sea. Despite several considerable deeps between 100 and the maximum of 459 m, the mean depth is only 65 m in the Baltic proper, 43 - 68 m in the Gulf of Bothnia and 38 m in the Gulf of Finland (Voipio 1981). The connection between the North Sea and the Baltic has its deepest passage, 18 m, through the Danish straits. The Sound, between Denmark and Sweden, is a rather flat and shallow area with a sill at a depth of only 8 m.

Hydrography

One of the most striking features of the Baltic is its low and stable salinity ($S = 0.5 - 1.0 \text{ ‰}$). This is a result of the positive water balance and a restricted water exchange between the Baltic sea and the North sea. The sum of run-off and precipitation exceeds the evaporation rate, while the inflow of more saline marine water is partly blocked by the shallow thresholds in the estuary. However, a vertical gradient of the salinity is formed in the deep basins of the sea dividing the water column into an upper layer (0 - 70 m) of brackish water and a lower layer of higher salinity. The existing halocline between these layers is very stable and allows no vertical exchange of water. Renewal of the deep waters is slow and occurs only temporarily through inflow of oxygen-rich water from the North Sea. The residence time of the water in the central deeper basins of the Baltic is reported to be between 25 and 40 years (Melvasalo 1981).

The great vertical stability of the water column and the poorly renewed deep water enhance stagnant conditions in the deeper basins. In 1975, the area of the sea bottom with reduced conditions for life was reported to be about 100,000 km², which is the maximum value observed so far.

Meteorological conditions

The Baltic extends from 54° N to 66° N. Intensive changes in the weather between the seasons of the year are typical of regions at these latitudes. Furthermore, there are large climatic differences between the northern and southern parts of the Baltic during the winter. While subarctic conditions exist in the North, mild marine conditions prevail in the South. The ice-cover (in the archipelagos) may last half a year in the northern part of the Gulf of Bothnia, while near-coastal ice formation generally occurs for a period of only one to two months in the southern Baltic.

Temperature gradient in surface water

Depending on the high incident solar radiation during the summer, the upper layer of the water column is stratified with a vertical temperature gradient. The surface water down to 20 m depth is warmed and usually reaches temperatures between 15 and 18°C at the open sea. This layer of warm surface water is followed by a layer of winter-cold (0 - 3°C) surface water down to the halocline (70 m depth), which persists throughout the year. Below the halocline water temperatures are constantly 3 - 5°C.

The Baltic ecosystem

The natural environment of the Baltic can be described as a simple ecosystem with just a few dominant species. Due to the low salinity and the osmotic stress, only a limited number of marine and fresh-water organisms and a few brackish-water specialists are established in the Baltic sea, for instance of the some 1500 macroscopic animals off the Norwegian coast, only some 70 species are to be found in the central Baltic. Many of the Baltic species are characterized by smaller size and slower growth than species in fully marine water (Jansson 1980). The most diversified communities live on the hard bottoms. The upper vegetative zone is dominated by algae of the genera Cladophora and Ceramium. Below this zone, the perennial belt of the bladder wrack, Fucus vesiculosus, extends down to 8 m depth. The Fucus-belts cover important nursery grounds for fish like pike, perch, eel, brim, cisco and gobies.

While the vegetative cover on the hard bottoms consists mainly of algae, the animal biomass can be totally dominated by the blue mussel, Mytilus edulis. A more common clam is Macoma baltica which lives on the soft bottoms of the offshore areas together with the amphipods, Pontoporeia affinis and P. femorata.

The above mentioned species are also present in the Alaskan coastal waters as well as fish of the genera Coregonus, Myoxocephalus, Gadus, Platichthys and Clupea harengus (Elmgren et al. 1980a,b).

The Baltic natural system corresponds to a very sensitive living reservoir whose inhabitants have adapted to the osmotic stress of the brackish environment. But the environment and natural systems are subject to change. The Baltic ecosystem is stressed, not only by a low salinity and temperature, but also by heavy utilization of the natural resources, significant pollution load from land-based sources, eutrophication and reducing conditions in the deep waters. These influences are able to change the structure of the Baltic ecosystem to a more simple one.

OIL POLLUTION LOAD IN THE BALTIC SEA

The aim of pollution load statistics and estimates is to assess the seriousness and the scale of the inputs from different known and possible sources and by means of these to try to map the problem areas. A recent compilation of the pollution load into the Baltic Sea area shows that petroleum hydrocarbons (PHCs) may well occupy the fourth place on the list of the most important pollutants based on the total amount of inputs, namely after organic matter (BOD: 1,640,000 t/a), nitrogen (TOT-N: 940,000 t/a) and phosphorus (TOT-P: 48,000 t/a), (HELCOM 1987).

The oil pollution load in the Baltic has declined since the 1970s, when the total input of PHCs was estimated to be between 50,000 and 100,000 tons per year (Melvasalo 1981; Jensen and Jørgensen 1984). The most recent estimates made during the 1980s fall within the range of 21,000 - 66,000 tons per year (Enckell 1986; HELCOM 1987) (TABLE 2).

According to recent figures, the input of PHCs from sea transport may be between 2 and 24 % of the total load, while inputs from other sources, e.g. from land-based sources via rivers alone may be much larger (38 - 67 %).

TABLE 2. Compilation of measured and estimated oil pollution load on the Baltic sea (after Enckell 1986).

SOURCE	INPUT (tons/year)

URBAN DISCHARGES	
- municipalities	3,000 - 9,000
- stormwaters	1,000 - 5,000
INDUSTRIAL DISCHARGES	
- refineries	163
- steelrolling mills	307
- others	400 - 1,000
SEA TRANSPORT	
- reception facilities	100 - 200
- shipping	160 - 6,500
- accidents	200 - 9,000
OIL/GAS PLATFORMS	< 5
RIVERS	14,000 - 25,000
ATMOSPHERIC INPUT	1,000 - 10,000

TOTAL	21,000 - 66,000

Estimates of the oil pollution load involve considerable uncertainties (suggested by the authors). It is very difficult to measure the scale of all these oil inputs and to reach far going conclusions about the seriousness of the oil pollution from the various sources. E.g. in many of the input surveys no distinction is made between mineral oils and fatty oils of natural origin. Losses from shipping are estimated as total volume-based amounts while contributions from other sources are measured as hydrocarbons. These are some reasons why the comparison of inputs from different sources can be misleading.

The decline of oil input to the Baltic may reflect a trend of decreasing oil consumption together with new more efficient measures to reduce oil inputs. The recent estimate of oil input to the world's oceans has been estimated to be about 3,3 million tons per year (according to the survey of the National Academy of Sciences in the USA). Comparing the load of the Baltic with that of the oceans, it can be concluded that the Baltic receives only about 2 % of the total oil input, but given on a per unit volume basis, the degree of oil pollution in the Baltic may be as high as one hundred times that of the world seas generally (Monitor 1988).

The most severe sources of oil pollution to point out are the short-lived spills from shipping. These are often visible and easily to detect and follow up. An oil spill can drift long distances, decompose only slightly and thus affect the natural systems on its way. But what are the long-term effects of constant and chronic inputs e.g. from land-based sources and atmosphere, which possibly are much larger?

Despite the uncertainties in the input estimates oil pollution must be classified as a problem in the Baltic. The probability of oil pollution is high because of intensive shipping, increasing offshore oil production and the heavy industrialization of the Baltic states. The operational (non) accidental discharges from shipping are still out of control as are the discharges of oil-based drilling muds and lubricants from offshore oil production and exploration. The oil production platforms are installed in the sea areas of Poland and West Germany. But there are several exploratory wells in the Kattegat and the Baltic, which have been drilled by Denmark and Sweden. New wells will be expolarated, especially off the island of Gotland in the Swedish sea area, where about 200,000 barrels of crude oil of good quality was reported to be found in April of this year.

There are at least several factors, mainly due to the basic features of the Baltic Sea, that make this sea more susceptible to damage.

FACTORS DETERMINING THE SEVERITY OF OIL POLLUTION

Constant oil pollution load from different sources may result in accumulation of oil residues in the Baltic Sea basin because of the specific hydrographic features of this sea.

- (1) The Baltic is a cold sea. The winter cold surface water exists throughout the year below 20 m depth. In this water layer the degradation of oil, especially its acutely toxic, volatile aromatic hydrocarbons is very slow.
- (2) The low salinity may play a part in prolonging the residence time of the lighter aromatic compounds (Elmgren et al. 1980a).
- (3) When an oil spill occurs in a shallow coastal area with an archipelago (typical of the Baltic), oil will be removed and decomposed slowly because of low exchange rates, low wave energy conditions and near zero tidal energy.
- (4) There are also special problems connected with oil spills in ice-covered sea areas during the winter. Firstly, the present measures available to collect oil from ice-covered seas have proved to be inefficient. Oil may decompose very little among ice. It may drift with ice massives from place to place and split into small spills. So an oil spill accident will be acute for several months until the ice melts.
- (5) When oil residues finally reach deeper bottoms below 70 m depth, the degradation of oil is prolonged because of reducing conditions (oxygen deficiency) in this deep water layer.
- (6) Residence times in deep waters are estimated to be as long as 25 - 40 years. As the conditions in these water layers appear to be rather permanent, oil residues in the sediment may accumulate for decades.

OCCURRENCE OF PETROLEUM HYDROCARBONS (PHCs)

The following description of the distribution of PHCs in the Baltic marine environment is mainly based on the review of Andruliewicz and Rohde (1987).

PHCs in water

A technique to measure total concentrations of hydrocarbons (THC) by ultraviolet fluorescence spectrometry (UVF) at an excitation wavelength of 310 nm have been used as a screening method to detect possible PHC contamination in the Baltic.

PHCs enter the Baltic Sea basin from the air, ships and land-based sources, of which the latter source is possibly the most important one. This is clearly seen from higher PHC

concentration in coastal waters. Based on UVF measurements in the Baltic Sea, PHCs occur in concentrations between 1.0 and 12 $\mu\text{g l}^{-1}$ in coastal waters, while the average concentration of PHCs in the Baltic has been reported to be within the range from 0.2 to 2.0 $\mu\text{g l}^{-1}$ (TABLE 3). PHC concentrations in the Baltic sea are about three times higher than the mean values for the North Atlantic.

TABLE 3. PHC concentrations in the Baltic Sea water (based on UVF measurements of THCs)

	Concentration ($\mu\text{g l}^{-1}$)
Coastal waters	1.0 - 12.0
Open sea (average range)	0.2 - 2.0
surface (mean)	1.3
subsurface (mean)	1.8
bottom (mean)	1.1
Surface microlayer	13.0 - 26.0
(Enrichment factor**)	(10.0 - 20.0)
** Enrichment factor = $\frac{\text{Conc. in microlayer}}{\text{Conc. in surface water}} - 1$	

Measurements of the PHC concentration in the uppermost micrometres of the Baltic Sea have been carried out since 1977. During the 1980s the concentrations of PHCs were normally within the range from 13 to 26 $\mu\text{g l}^{-1}$, which is about three times higher than the corresponding values for the North Atlantic. However, the mean enrichment factors for PHCs are the same for the Baltic and North Atlantic.

PHCs in sediments

The amount of hydrocarbons in sediments may vary considerably depending on the composition of the sediment (proportion of organic vs. mineral matter) and the redox conditions.

Monitoring of PHCs in sediments was carried out in the coastal area of southern Finland during 1987 - 1988. The sea bottom of the studied area represents a shallow and erosive sea floor with very heterogenic sediment composition. PHCs in the uppermost layer of the sediments showed a significant correlation with the content of dry matter (dm %). The concentrations of total hydrocarbons (THCs) were between 100 and 350 $\mu\text{g g}^{-1}$ in the samples with low content of dry matter (4 - 15 %). In the samples with higher content of dry matter

(15 - 70 %), THCs were generally found to be between 10 and 100 $\mu\text{g g}^{-1}$. Aliphatic hydrocarbons were also measured in the samples, which contained over 200 $\mu\text{g g}^{-1}$ of THCs. The concentrations of aliphatic hydrocarbons of the C15-C30 fraction were within the range from 5 to 24 $\mu\text{g g}^{-1}$. The concentration of unresolved complex mixture (UCM) in the same samples varied between 0 and 65 $\mu\text{g g}^{-1}$ (Hirvi 1989, in prep.). It must be noted that this study was carried out after an oil spill incident caused by the tanker Antonio Gramsci in the Gulf of Finland in 1987 (see FIGURE 2). However, no contamination could be detected in the sediment samples collected from the coastal sea floor. Thus, PHC concentrations observed in this study represent normal values in sediment in the Gulf of Finland (Poutanen et al. 1982).

Total hydrocarbons in sandy sediments from relative clean areas of the southern Baltic were found in concentrations between 10 and 30 $\mu\text{g g}^{-1}$ (dw), whereas sediments from polluted areas contained up to 130 $\mu\text{g g}^{-1}$ of total hydrocarbons. Aliphatic hydrocarbons of the fraction C15 - C30 in sandy sediments from the southern Baltic varied between 0.5 and 12.5 $\mu\text{g g}^{-1}$ depending on the degree of pollution and the degree of anoxia (Andrulewicz and Rohde 1987) (TABLE 4). These values are low compared to those found in the sediments in the Gulf of Finland.

TABLE 4. Aliphatic hydrocarbons in sandy sediments collected from the southern Baltic (sum of C15 - C30 fraction, $\mu\text{g g}^{-1}$, obtained by GC).

sediment type	AHCs
Coarse sand	0.65
Sand	0.45
Sand, non-polluted	0.20
Sand, polluted	4.30
Silt-clay, anoxic	2.70
Silt-clay, anoxic	12.70

Paraffin-naphthene hydrocarbons in sediments from polluted coastal areas may be present in very high concentration depending on the distance from a pollution source. This was clearly demonstrated in a monitoring of PHCs in sediments from seventy sites along the coast of Sweden in 1982. P-N-hydrocarbon concentrations in samples of surface sediment layers collected within a 20 km radius of major towns and industrial plants were five times those found in areas 50 km or more from these

pollution sources. The concentrations of p-n-hydrocarbons in the sediments near the pollution sources were within the range of 500 to 3,600 $\mu\text{g g}^{-1}$ (Mattson and Lehtinen 1985). The results of this study are of special interest, because the same sampling sites were studied in the mid 1970s. It could be concluded that on the average PHC levels in sediments have increased since the 1970s. However, in regard to the general decreasing trend of estimated oil pollution load in the Baltic sea area, the increased PHC levels may rather be a result of gradual accumulation in sediments than of an increase of oil inputs into the Swedish coastal waters since the 1970s.

PHCs in organisms

Oil residues in biota, especially in macrozoobenthos, have been investigated in a case of oil spill. Indicator organisms viz. the common blue mussel, *Mytilus edulis* and the Baltic clam, *Macoma baltica*, have been used to study the degree and extent to which oil pollution (from an oil spill) affected marine life.

During 1987 - 1988, the coastal sea area of southern Finland was investigated for the purpose of studying the environmental effects of the large oil spill caused by the tanker Antonio Gramsci in early 1987. Chemical analyses of the biota showed that PHCs were present in the samples of blue mussel and Baltic clam. PHC levels were generally higher in the second-year samples. Oil residues were not found in the sediment samples collected from the same sea area. It must be noted that the data on these analyses are in preparation and the study is still in progress. The PHC levels in the organisms studied have been summarized in TABLE 5.

TABLE 5. Levels of total hydrocarbons (THCs) and aliphatic hydrocarbons of the C15-C30 fraction (AHCs) and UCM in biota collected from the coastal sea of southern Finland during 1987-1988, (mean concentration and range, $\mu\text{g g}^{-1}$ dry weight; THCs obtained by UVF and AHCs by GC).

Organism	THCs	AHCs	UCM
	mean (range)	mean (range)	mean (range)
<i>Mesidotea entomon</i>	105 (15- 220)	6.0 (2-10)	30 (15- 40)
<i>Lymnea sp.</i>	395 (50- 730)	5.5 (1-14)	190 (40- 500)
<i>Macoma baltica</i>	838 (200-2,200)	4.5 (3- 9)	375 (0-1,440)
<i>Mytilus edulis</i>	1,210 (230-2,870)	3.5 (2- 7)	365 (40- 810)

These results suggest that the coastal sea area of southern Finland receives a constant input of PHCs, e.g. from the Neste refinery in Porvoo. The output of oil into the sea from these works has been measured at 14 tons per year (Talsi 1986). The intensive sea transport and tanker traffic to the refinery has also resulted in some serious accidents. The levels of PHCs in biota as presented above are higher than the normal values to be found in this sea area, which indicates that oil residues from the oil spill in 1987 are still present.

Budgets and balances for PHCs

The total input of PHCs in the Baltic may be between 21,000 and 66,000 tons per year. According to the average range of PHC concentrations found in the Baltic Sea water the amount of PHCs in the total water volume of the Baltic basin is somewhere between 5,000 and 45,000 tons. The amount of PHCs accumulated in the surface film of the Baltic Sea can be estimated at 2 - 3 tons.

The estimates of total inputs of PHCs to the Baltic Sea still suffer from many gaps and uncertainties. That is why it is not possible to calculate the budget (inputs against outputs) for the whole Baltic Sea. However, some results of a study in which inputs and outputs of PHCs were calculated in the Danish Kalundborg fjord area of 54 km² in the southern Baltic are available (Jensen 1983). The main conclusions to be drawn from this study were that the inputs of PHCs (23 tons) corresponded to that of the outputs (21.7 tons). However, the total PHC deposit in the sediments was measured to be 6.2 tons per year of which 4.9 tons were accumulated and only 1.3 tons were degraded, which means that about 75 % of the PHCs deposited was accumulated. This study demonstrates the general tendency observed in the Baltic Sea area for PHCs to be decomposed very slowly or not at all in sediments under reducing conditions.

OIL SPILLS

The oil pollution within the Baltic Sea area has been connected with accidental oil spills. Based on the environmental study of these spills the oil has been predicted to have considerable local effects, mainly on birds and coastal benthic communities (Kineman et al 1980; Pfister 1980; Vainio et al. 1987). The large spills that occurred at open sea have drifted long distances, decomposed only slightly, and caused severe pollution along the coasts.

Sea traffic through the Baltic Sea is heavy, both with respect to the frequency of ships and to tonnage. The largest tankers, which are allowed to enter the Baltic via the shallow

and narrow entrance, have sizes of up to 160,000 tons (DW). None of these larger tankers have been involved in an accident as yet, but the risk of grounding and/or collision is obvious because of

- (1) shallow and imperfectly sounded waters, e.g. Danish straits and Sound and all entrances to major ports
- (2) meteorological conditions, poor visibility during most of the year
- (3) subarctic conditions and ice-cover
- (4) high calling frequency of ships (estimated at least 200,000 port visits per year in the whole Baltic)

In 1986 the amount of oil and refined products transported in the Finnish coastal waters was calculated at 25 million tons. Tanker traffic to the Finnish ports amounted to 2,700 visits and the total number of ship visits exceeded 23,000. From the data on Finnish sea transport it can be estimated that there may be more than 200,000 visits of ships to the Baltic ports and the amount of transported oil and refined products must be at least 175 million tons per year at the Baltic Sea. Per unit of area the amount of oil transported was about 500 tons per km².

The Finnish oil spill statistics show that in 1987 there were a total of 2,311 leakages or spillages of oil in Finland, of which 381 occurred in water areas, where 26 spills were caused by tankers and 129 by other or unknown ships. It can be concluded that oil spills are a permanent phenomenon in the Baltic Sea. The largest oil spills that have occurred in the Finnish territorial waters are shown in FIGURE 2. There have been 27 large oil spills along the Finnish coasts during 1969 - 1987. The total (known) amount of oil influenced the Finnish coastal waters is about 8,000 tons.

There have been two large oil spills of over 5,000 tons in the Baltic Sea. The largest spillage was caused by the British tanker Globe Assimi off the Lithuanian coast of the USSR in 1981. The tanker was totally wrecked and about 16,500 tons of heavy fuel oil and 230 tons of bunker oil were spilled into the sea. It could be estimated that about 4,000 tons of oil was left in the marine environment. An environmental study showed no evidence of biological damage or increased PHC levels in the open sea water. The second largest oil spill took place in 1979 off the Latvian coast of the USSR. The Soviet tanker Antonio Gramsci ran aground and about 5,000 - 6,000 tons of crude oil was spilled. The oil drifted hundreds of kilometres northwards and caused damage to birds in the Swedish and Finnish

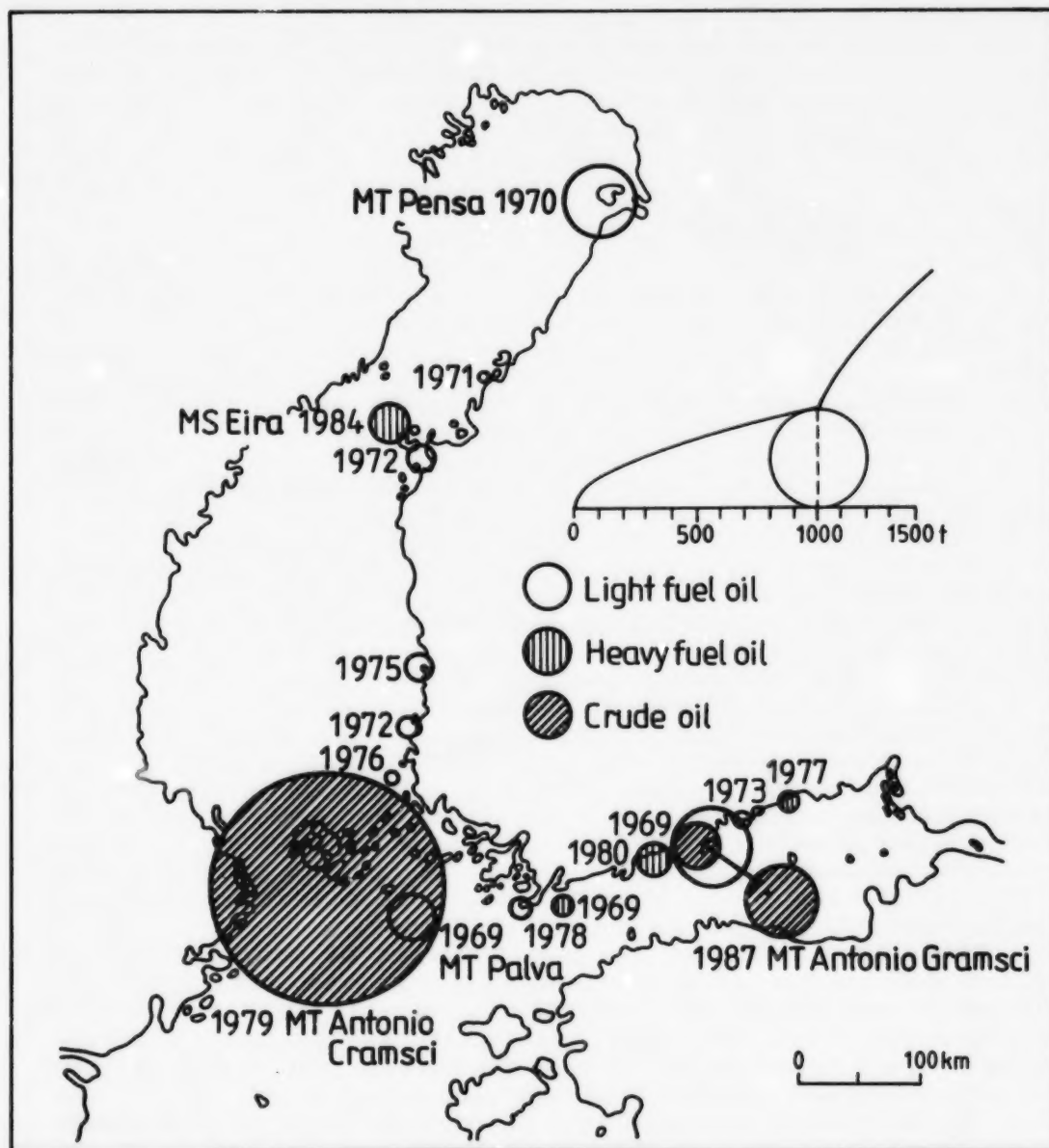


FIGURE 2. The largest oil spills in the Finnish waters of the Baltic Sea during 1969-1987.

archipelagos.

Every oil spill incident will be different. Biological damage is not always relative to the amount and the type of oil spilled. In 1976, an oil spill of about 10 tons (from tank washing ?) caused severe damage to seabirds off the island of Öland in the Swedish coastal sea. At least 33,000 and possibly as much as 66,000 long-tailed ducks and other birds were killed. In February of 1987, the grounding of Soviet tanker Antonio Gramsci off the southern coast of Finland caused a spillage of about 570 tons of crude oil. The oil drifted with ice-fields in the Gulf of Finland and threatened sea birds during several months, but only about 40 birds were killed by the oil. However, the oil affected fish and fisheries.

The Antonio Gramsci oil spill incident was acute for the first half of 1987. Soon after the spillage, the oil mixed with drift ice. All attempts at collecting the oil (oily ice) were stopped because of the low effectiveness of the oil recovery under the prevailing ice conditions. During the winter, the oil decomposed only slightly and it split into several small spill areas. When the oily ice-fields finally melted, the oil was released to the sea and degraded by stormy wave fields. The combatting succeeded in collecting 100 tons of oil at sea and 37 tons of oily wastes from the shores. The fate and bulk loss of this oil spill was calculated and estimated at about 300 tons as shown in TABLE 6.

TABLE 6. The fate of 570 tons of crude oil spilled by Soviet tanker Antonio Gramsci in the Gulf of Finland in 1987.

Spreading area	2,500 km ²	
Collected at sea	100 tons	80 tons in Feb.
Collected from shores	10 tons	37 tons of oily wastes
Evaporation, February	114 tons	20 % x 570 tons
Evaporation, March-April	38 tons	10 % x 376 tons
Evaporation, May-June	34 tons	10 % x 338 tons
Sedimentation, winter	< 1 ton	
Dissolution, winter	< 1 ton	

BULK LOSS	298 tons	272 tons were left in the environment

ACTIONS REQUIRED

Scientific knowledge

There are several unresolved problems and gaps in our knowledge about oil (spills) and oil pollution control in the Baltic Sea area. According to the general conclusions in HELCOM (1986), the actions are required in the following fields of scientific knowledge. More studies are needed (1) on atmospheric and land input of petroleum hydrocarbons into the Baltic Sea, and (2) on the concentration of petroleum hydrocarbons (PHCs) and especially on the polynuclear aromatic hydrocarbons (PAH) fraction in sediments and biota. More studies are also required (3) on the occurrence of PHCs in all compartments of the Baltic Sea for purpose to set up realistic budgets and balances for these hydrocarbons. More efforts should be exerted (4) to develop specific, accurate and relatively simple analytical methods to determine the most persistent and toxic individual-components and groups of compounds originating from oil.

Research preparedness

The large oil spill incidents that occurred in the Baltic Sea have demonstrated that Finland and also other Baltic states have a lack of research preparedness generally, e.g. they lack research contingency plan and organisation, as well as suitable research equipment to maintain independent research activity in a case of an oil spill incident.

The environmental protection activities of the Baltic Sea are organized within the Baltic Marine Environment Protection Commission - the Helsinki Commission (HELCOM), which was established in Helsinki in the mid 1970s. The Helsinki Commission includes three working Committees, namely the Scientific-Technological, Maritime and Combatting Committee. Exchange of information on spillages of oil and other harmful substances is the task of the Combatting Committee.

In 1988, Finland presented "a preliminary proposal with guidelines for the biological and chemical follow-up studies following oil and other chemical spillages" in the Baltic Sea area. This proposal will be completed within the Combatting Committee and presented to the Helsinki Commission in the form of a recommendation. The proposal includes the most necessary tasks and research items that should be implemented during the acute phase of an oil spill incident divided into the following main actions;

- (1) Coordination of research work
- (2) Technical investigations
- (3) Physico-chemical investigations
- (4) Biological investigations
- (5) Documentation and strategy for continuing research work

Oil combatting

According to a recommendation accepted in the meeting of the Helsinki Commission in 1980, the following goals were set for the development of the national contingency organisations for oil combatting;

- (1) be able to combat an oil spill of 10,000 tons within 10 days
- (2) a combatting team should be able to start within two hours after alarm
- (3) a combatting team should reach a spill place/area within six hours after start

The capacity for oil recovery in Finland can be calculated at 1,600 cubic meters per day. This is estimated from the amount of LORI-oil brushers (for ice conditions) or similar systems installed on ten oil combatting ships. The estimate is based on a maximum total recovering capacity of 560 cubic meters per hour in realistic conditions for the effective recovering time available in usual conditions. The tank capacity of the abovementioned 10 vessels totals 1,700 cubic meters. A new oil combatting ship (35 m length) will be ready in 1989. Furthermore, there are almost 50 vessels of e- and f-class size available for oil combatting by the regional authorities (e.g. fire-services). Combatting material in stores can be listed as follows; 8 km sea boom, 12 km coastal boom, 34 different kinds of oil recovery equipment, 17 work platforms, 45 containers, tanks, protective material etc.

The oil combatting contingency organisation in Finland is able to control small spills at a regional level. The problems are connected with large oil spills over 100 - 500 tons and especially when they occur in ice-covered sea areas. Under subarctic conditions, the recovering capability may decrease considerably. And none of the Finnish combatting vessels has in fact been designed to work under ice conditions.

CONCLUSIONS

The Baltic Sea is an isolated and sensitive brackish water environment. The ecosystem of the Baltic is not only stressed by a naturally low salinity but also by severe pollution load from air, sea transport and land-based sources, e.g. nutrients, chlorinated hydrocarbons, heavy metals and petroleum hydrocarbons (PHCs).

The total load of oil pollution in the Baltic Sea has been estimated at between 21,000-66,000 tons per year, which is about a hundred times higher than that of the world seas on a

per unit volume basis. The average concentrations of PHCs in the Baltic Sea water have been measured at 0.2-2.0 $\mu\text{g l}^{-1}$, which is about three times higher than the mean concentration to be found in the North Atlantic.

The problems are involved with oil spills over 100 tons, especially when they occur in an ice-covered sea area. There are no effective measures and oil recovering equipment for combatting of oil under ice conditions. Oil will decompose very little, drift long distances with ice, split to small spills and cause severe pollution along coasts. The degradation of oil residues in the Baltic Sea basin is affected by several factors, e.g. winter-cold water layer below 20 m depth persisting throughout of the year and reducing conditions in the deeper bottoms. Environmental studies of large oil spills in the Baltic Sea have shown that birds and coastal benthic communities are the parts of the ecosystem worst affected.

Nowadays measures against oil pollution load are mainly concerned with spillages from ships. New effective measures must be developed to combat oil in ice-covered sea areas. Furthermore, it has been proposed that the research organisations involved should act more efficiently in cases of large oil spills. A recommendation will be prepared, which includes guidelines for the biological and chemical follow-up studies following oil and other chemical spillages.

The basic features of the Baltic described in this review make this sea susceptible to damage. The degree and probability of oil pollution is high because of intensive shipping, heavy industrialization of the Baltic states and increasing offshore exploration and oil production. More studies are required to complete the background data on levels of PHCs in sediment and biota, and to increase the present knowledge on pathways, fate and inputs in order to map the occurrence and to set up realistic budgets and balances of PHCs, especially in those areas of the Baltic Sea which are affected by chronic oil input. Because of the gaps in our knowledge, it is not yet possible to document any widespread negative effects of PHCs on biota in the Baltic marine environment.

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**VESSEL DESTRUCTION:
A VIABLE RESPONSE OPTION FOR ISOLATED AREAS**

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ABSTRACT

On numerous occasions over the last ten years, the United States Government used its authority under the Federal Water Pollution Control Act and the Intervention on the High Seas Act to resolve vessel pollution incidents. The Federal On-Scene Coordinator was granted authority to intervene from the Commandant, U.S. Coast Guard, after providing information on the vessel, cargo, damage, owner's actions, recommended actions. This paper will review several vessel incidents which occurred in Alaskan waters and lead to intervention authority being granted to remove, burn in place, or sink the vessel to resolve the pollution problem. Specific cases which are discussed include the M/V RYUYO MARU #2 (1979), the M/V LEE WANG ZIN (1980), the F/V DAE RIM (1981), and the M/V AOYAGI MARU (1988).

DISCLAIMER

The opinions and recommendations presented in this paper are those of the authors. Content should not be construed as representing the U.S. Coast Guard or any other government agency.

The United States is a party to both the International Convention Relating to Intervention on the High Seas in Cases of Oil Pollution Casualties, entered into force on May 6, 1975, and the Protocol to the Convention Relating to Intervention on the High Seas in Cases of Marine Pollution by Substances Other Than Oil 1973, entered into force on March 30, 1983. The Convention and Protocol were implemented into U.S. Law (33 U.S. Code 1471-1487) by the Intervention on the High Seas Act of 1974. The U.S. also enacted national legal authorities for mitigating pollution disasters on the high seas or navigable waters of the U.S. under Sections 311(c) and (d) of the 1972 Federal Water Pollution Control Act (FWPCA), as amended in 1978 (33 USC 1321(c) and (d)), and under Section 104 (a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, (42 USC 9604).

The FWPCA and CERCLA each focus on a different pollution concern. However, each provides legal authority which can be used to intervene and take steps to protect U.S. Waters in response to vessel related pollution incidents. Even though the

International Convention and Protocol are not directly applicable within the Navigable Waters of the United States, the procedures outlined therein are to be followed to the extent possible when intervention is conducted under the authorities of the FWPCA and CERCLA.

Under U.S. Law "intervention" is considered to be any detrimental action taken against the interest of a vessel or its cargo without the consent of the vessel's owner or operator. It includes, but is not limited to, any of the following measures:

- a. salvage operations of a vessel or its cargo which are necessary to reduce the pollution or pollution threat;
- b. transfer of oil or hazardous substances to other tanks or other ships or barges;
- c. deployment of equipment for containing or dealing with a spillage;
- d. removal or destruction of a vessel;
- e. disposal or destruction of the cargo on board;
- f. orders to the Master, owner, or operator of a vessel.

Under U.S. Law the authority to carry out the provisions of the Intervention on the High Seas Act has been delegated to the Commandant of the U.S. Coast Guard. The legal authority and resulting responsibilities include:

- a. coordination and direction of all public and private efforts for the removal or mitigation of the pollution or threat of pollution damage;
- b. the undertaking, either directly or indirectly, of the whole or any part of any salvage or other action which may be required;
- c. to remove and, if necessary, destroy the vessel and or cargo which is the source of danger.

It is important to recognize that under the International Convention and U.S. Law, only those measures that are reasonably necessary for prevention, mitigation, or elimination of the pollution threat are authorized. Unnecessary interference is to be avoided and intervention actions are to cease upon mitigation or elimination of the threat.

The primary focus of legal authority under the Intervention on the High Seas Act is to deal with threats of pollution beyond the Territorial Seas. Since Sections 311 (c) of the FWPCA and 104(a) of CERCLA also provide implicit authority for intervention on the high seas, they are also cited appropriately in the Commandant's authorization to intervene. The legal authority under Section 311(d) of the FWPCA is limited to intervention action upon the navigable waters of the U.S. which include the territorial seas and internal waters.

The legal authorities discussed up to this point have not just collected dust. The U.S. Coast Guard has used the authorities numerous times over the last ten years to mitigate or prevent pollution incidents.

While the immediate thought in many peoples' minds when intervention is mentioned is the destruction of a vessel, that has not always been the case. These authorities have been used

on several occasions to simply lighter cargos as in the M/V WELLWOOD (Florida, 1984) and the M/V ANANGEL LIBERTY (Hawaii, 1980), or to prevent a vessel from being towed into port as in the T/V PUERTO RICAN (California, 1984). The M/V WELLWOOD incident was the first case in the U.S. utilizing the authorities given under the Intervention on the High Seas Act.

It is important to remember that intervention action must be detrimental to the interest of the vessel or its cargo without the consent of the owner. In a case such as the T/V Barge 283, which capsized off Simeonof Island, Alaska in January 1989, the vessel's owners chose to take the vessel offshore and sink it rather than attempt salvage. Although the Coast Guard provided assistance in sinking the vessel, it was at the request of the owner, and intervention authority was not needed.

However, in isolated areas such as Alaska, the intervention authority has been frequently used to mitigate a pollution threat by destroying the vessel, its cargo, and or its bunkers. The primary reasons for these actions in this area are three fold. First, the vessels involved have been for the most part foreign flag vessels involved in the fishing industry or general cargo trade. Therefore, their limits of liability under the law are low and there is little incentive for their owners to take responsibility for any actions that would exceed these limits, even if for purely public image reasons. Secondly, the logistics involved with mounting a response to isolated areas immediately pushes the cost of actions beyond the limits of liability for most vessels and exceeds the criteria for a timely response. The final premise is that the rough coastline or terrain where the casualty may occur often precludes any other response option. To examine these reasons in more depth, several incidents will be discussed where intervention action resulted in vessel destruction.

M/V RYUYO MARU #2

The M/V RYUYO MARU #2, a 100 meter combination stern trawler/processing vessel grounded at St Paul Island, Alaska in November, 1979. The vessel went aground at the base of a 50 meter cliff that extended two kilometers to the East and four kilometers to the West. Surf conditions and water depths precluded any opportunity for vessels supporting salvage or bunker off-loading operations coming alongside.

In addition, the ship's engine room was flooded causing a loss of all ship's power and the grounding caused a release of ammonia from the refrigeration system. Concentrations of ammonia over 1000 ppm were found within the superstructure and cargo holds. Although a highline was rigged to off-load the 450 tonnes of fish products, nets, and other materials on board the vessel to gain access to the bunker tanks, the ammonia vapors and weather prevented this operation from taking place.

Due to these adverse conditions and the owner's refusal to take responsibility for pollution mitigation, the Commandant authorized intervention actions to minimize the threat. On November 22, with the assistance of a U.S. Navy Explosive

Ordnance Team, explosives were placed along the hull and in strategic locations in the superstructure and holds to ignite the 265 cubic meters of oil remaining on board, and to intentionally release any oil that did not burn. Because a storm passage was predicted for the evening of November 22, it was felt that any oil that escaped would be dissipated in the heavy surf before threatening environmentally sensitive areas.

M/V LEE WANG ZIN

In December 1979, the M/V LEE WANG ZIN, a bulk cargo vessel, capsized near Dixon Entrance, South East, Alaska. The vessel drifted with only the bottom hull exposed until it grounded near Ketchikan, Alaska. Here the vessel posed a significant threat of pollution to U.S. Waters. After determining that no survivors were trapped within the hull, the Commandant authorized intervention. An ocean dumping permit was obtained from the U.S. Environmental Protection Agency, and the vessel was towed to deep water in the Gulf of Alaska and sunk.

F/V DAE RIM

In March 1981 the F/V DAE RIM caught fire in the Bering Sea and was abandoned by its crew. The fire eventually extinguished itself and the vessel drifted until being taken in tow by another vessel. However, after being towed into the Gulf of Alaska, sea conditions put the towing vessel in extremis and the tow line was severed. The F/V DAE RIM then drifted until it grounded at Attu Island, Alaska. It was believed to have approximately 435 cubic meters of diesel oil on-board. The owners refused to take responsibility to mitigate the pollution threat to U.S. Waters. At this site the Aleutian Island National Wildlife Refuge would have been directly impacted from a spill. The U.S. Navy provided an Explosive Ordnance Detachment to place charges on the hull for in situ burning and a controlled release of oil not consumed by the fire. Due to sea conditions, a boarding party was unable to board the ship to determine the amount of oil remaining on board. A visual inspection by telescope indicated that two tanks apparently remained intact.

Several rounds from a Coast Guard Cutter's five inch gun resolved this problem. Six meter seas quickly dissipated any oil not burned.

M/V AOYAGI MARU

A more recent case of intervention was the grounding of the M/V AOYAGI MARU. On December 10, 1988 this 92 meter refrigerated cargo vessel was in the process of lightering fish products from a processing vessel near Akun Island, Alaska. When the two vessels broke away from each other, a line was caught in the screw of the M/V AOYAGI MARU and the vessel was pushed aground by heavy seas. On December 17, the vessel was declared a total loss by the hull underwriter. The insurers and owner's representatives agreed to remove the 120 cubic meters of diesel oil on board only if the cost of that action would be credited toward their limit of liability if the government chose to take further action. Their proposal did not address the estimated 245 cubic meters of bunker oil and lubricating oils that would have been

left on board the vessel. When the Federal On-Scene Coordinator refused to accept their conditions, the owner declined financial responsibility for any cleanup action. On December 28, the FOSC declared the incident a Federal cleanup activity.

The option chosen for the Federal response included a request for intervention authority for the purpose of burning the oil in place and preventing the chronic release of oil over a long period of time. To complete the operation the diesel oil contained in the forepeak tank was pumped to a support vessel. The flooded cargo holds were pumped dry and the insulation and decking that covered the double-bottom tanks were removed. Hose charges were then cut in half and placed longitudinally along the tank tops in each hold and covered with sand bags to direct charges downward. When detonated on March 19, 1989, the bunker oil that was pressed up in the tanks was released into the cargo hold. The diesel oil was then pumped into the cargo hold on top of the bunker oil and the entire ship was set afire with thermite charges. The fire aboard the ship blazed for two weeks with no sighted release of oil into the surrounding waters. The entire operation was conducted within the vessel's pollution liability limits.

SUMMARY

As shown in the above case studies, destruction of vessels is a viable response tool. This is especially true in areas such as Alaska, where other types of response resources are not readily available and the logistics involved in bringing them to the pollution scene makes them very costly. U.S. Coast Guard policy is to make every effort to provide the responsible party with the opportunity to conduct a proper cleanup and to control the source of pollution. However, at times this policy does not provide for a timely response effort either on the part of the responsible party, or the government if that party refuses to take proper actions. It is also not in the best interest of the taxpayers to be burdened with ultimately paying the difference between the seemingly low limits of liability for which the maritime industry is responsible and the actual costs of mitigating casualties when the Federal government is forced to take corrective actions.

It is recommended that future legislation be implemented to resolve several problems in this area. First, increase the limits of liability for vessels engaged in trade in isolated areas where response costs are inflated due to logistics and lack of competition. This would ensure that more adequate funds would be available to owners through insurers to conduct a proper salvage or cleanup. Secondly, require domestic, foreign, and joint venture fishing industries and other commercial industries supporting their activities in the Bering Sea to form a pollution response cooperative similar to the co-ops formed by the oil industry in other coastal areas. This action would ensure, to some degree, that adequate response equipment would be available in a timely manner. And thirdly, institute some method of providing an incentive for small vessels and companies operating

in remote areas to conduct proper response activities. Failure on the part of the owner to conduct an appropriate salvage or cleanup would limit or void their certificates, permits, or fishery allocations. Until owners or operators are financially forced to take more complete responsibility for marine pollution incidents, the U.S. Government will have to continue to take intervention action to resolve pollution incidents in remote areas.

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